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Multipole Polarizabilities and Long-Range Interatomic Forces for Two and Ten Electron Atoms.

Joseph Tracy Broussard
Louisiana State University and Agricultural & Mechanical College

Multipole Polarizabilities and Long-Range Interatomic Forces for Two and Ten Electron Atoms

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ABSTRACT

By means of time-dependent perturbation theory, multipole polarizabilities of two and ten electron atoms have been calculated. All polarizabilities have been calculated as a function of imaginary frequencies from an external field perturbation. The calculations are done by means of an uncoupled Hartree-Fock method to obtain results with and without correlation. An interchange theorem eliminates the need for wavefunctions that include electron correlation. From the frequency-dependent polarizabilities, long-range forces are calculated; these include dipole-dipole, dipole-quadrupole, dipole-octupole, and quadrupole-quadrupole interactions. Dipole-dipole interactions give the usual London dispersion coefficients of $1/R^6$; dipole-quadrupole give $1/R^8$ interactions, and dipole-octupole and quadrupole-quadrupole give the $1/R^{10}$ contribution to the long-range interactions.

The double perturbation theory formalism is needed whenever polarizabilities are to be calculated by means of an uncoupled Hartree-Fock procedure; the external field is one perturbation and the electron correlation correction is the other perturbation.

In calculating the long-range interactions, we have used the one-center method, which involves the calculation of an integral over the product of the frequency-dependent polarizabilities of the two interacting atoms.

I. INTRODUCTION

The rather broad area of intermolecular forces is usually divided into four regions characterized by the distance between the interacting atoms.[1] There are short-range forces where electron cloud overlap is considerable, giving rise to repulsive interactions. At slightly larger distances between atomic centers, there are intermediate-range forces where both electron charge overlap and electrostatic induced multipole forces are present. At large distances where electron clouds no longer overlap, only multipole interactions exist. Even in spherically symmetric atoms there are instantaneous multipoles due to quantum mechanical zero point motions which can lead to induced multipole interactions. The energies of interactions which describe this region are usually called long-range "forces". Following standard usage we shall use the word "force" for the interaction energies. We shall be concerned with these long-range interactions. The last region is that of very large separations, i.e., distances larger than the wavelength corresponding to excitation energies of the atomic systems. Here retardation effects due to the finite speed of electromagnetic waves must be considered in addition to the multipole interactions. However, the interaction is so small at such separations that it has mainly academic interest.

Many advances have been made in recent years to improve the calculation of forces between atomic systems at separations large compared with the size of the atoms. Most of these advances have resulted from a recognition that the two-center molecular problem can be put into the form of two one-center problems when the atomic overlap

can be neglected.[2] The one-center solutions can be found by means of the various methods developed for calculating the response of an atom to an external perturbation. This interaction is conventionally represented as an asymptotic series expansion in inverse powers of the separation, R. The leading term, known as the London dispersion force, is the induced dipole - induced dipole interaction which varies as R^{-6}. Successive terms are the induced dipole - quadrupole interactions decreasing as R^{-8}, and the induced dipole - octupole and induced quadrupole - quadrupole terms both of which contribute to the R^{-10} interaction.

II. GENERAL THEORY

The potential energy, U, between two neutral atoms can be written in a number of different forms if the charge distributions of the interacting atoms do not overlap. The potential between a pair of spherically symmetric atoms I and II at a distance R apart is[1]

$$U = \sum_{\ell=0}^{\infty} \sum_{L=0}^{\infty} U_{\ell L}/R^{\ell+L+1} \tag{1}$$

The form of $U_{\ell L}$ depends upon the choice of coordinate systems for atoms I and II, but if the coordinate frames are parallel and the interaction is chosen with the z-axis along R, then we have[3] (using atomic units in which $\hbar = m_e = e = 1$; distances are in units of the Bohr radius and energies in Hartree units, 27.21 eV)

$$U_{\ell L} = \sum_i \sum_j \sum_{\mu=-\lambda}^{+\lambda} \frac{(-)^L 4\pi(\ell+L)!\, r_i^{\ell} Y_\ell^{\mu}(\hat{r}_i)\rho_j^{L} Y_L^{-\mu}(\hat{\rho}_j)}{[(2\ell+1)(2L+1)(\ell-\mu)!(\ell+\mu)!(L-\mu)!(L+\mu)!]^{\frac{1}{2}}} \tag{2}$$

where λ is the smaller of ℓ and L.

Each of the $U_{\ell L}$ interactions arises from the interaction between a 2^{ℓ}-pole moment of atom I with tensor components

$$M_\ell^m(I) = \sum_i r_i^{\ell} Y_\ell^m(\hat{r}_i) \tag{3}$$

and a 2^L-pole moment of atom II with tensor components

$$M_L^M(II) = \sum_j \rho_j^L Y_L^M(\hat{\rho}_j) \tag{4}$$

where r_i and ρ_j are position coordinates for electrons in atom I and II respectively. Likewise $\hat{r}_i$ and $\hat{\rho}_j$ are the angular coordinates appropriate for the same electrons.

The effect of the interaction potential U on the system can be calculated using perturbation theory. The eigenfunction Ψ of the total system satisfies the Schrödinger equation

$$\mathcal{H}\Psi = (\mathcal{H}_o + U)\Psi = (\mathcal{H}_I + \mathcal{H}_{II} + U)\Psi = E(I,II)\Psi \tag{5}$$

with $\mathcal{H}_I$ and $\mathcal{H}_{II}$ being the Hamiltonians of atoms I and II respectively.

Using the Rayleigh-Schrödinger perturbation expansion[4], we write

$$\Psi = \sum_{n=0}^{\infty} \lambda^n \psi^n \tag{6a}$$

$$E(I,II) = \sum_{n=0}^{\infty} \lambda^n E^n(I,II) \tag{6b}$$

Substituting equations (6a) and (6b) into equation (5) and equating coefficients in like powers of λ; the zero, first, and second order equations are, respectively,

$$[\mathcal{H}_o - E_o(I,II)]\psi^o = 0 \tag{7a}$$

$$[\mathcal{H}_o - E_o(I,II)]\psi^1 + [U - E^1(I,II)]\psi^o = 0 \qquad (7b)$$

$$[\mathcal{H}_o - E_o(I,II)]\psi^2 + [U - E^1(I,II)]\psi^1 - E^2(I,II) = 0 \qquad (7c)$$

The zero-order solution for non-overlapping atoms is the product of the zero-order wavefunctions of the separate unperturbed atoms

$$\psi^o = \varphi_I^o \phi_{II}^o \qquad (8a)$$

and

$$\mathcal{H}_I \varphi_I^o = E_I^o \varphi_I^o \qquad (8b)$$

$$\mathcal{H}_{II} \phi_{II}^o = E_{II}^o \phi_{II}^o \qquad (8c)$$

From equations (7b) and (7c) we obtain respectively

$$E^1(I,II) = \langle \psi^o | U | \psi^o \rangle \qquad (9)$$

and

$$E^2(I,II) = \langle \psi^o | U | \psi^1 \rangle \qquad (10)$$

The interaction energy correct to second order in U is then given by

$$E(R) = E^1(I,II) + E^2(I,II) \qquad (11)$$

where for notational convenience we use E(R) in the place of $E(I,II) - E_I^o - E_{II}^o$.

Using equations (9) and (10), equation (11) can be written as

$$E(R) = \langle\psi^o|U|\psi^o\rangle + \langle\psi^o|U|\psi^1\rangle \quad . \qquad (12)$$

For spherically symmetric non-overlapping atoms $E^1(I,II)$ vanishes, and equation (12) becomes

$$E(R) = E^2(I,II) = \langle\psi^o|U|\psi^1\rangle \quad . \qquad (13)$$

Thus, to obtain E(R) we only need to solve equation (7b) for ψ^1. To simplify equation (7b), we introduce

$$\psi^1 = \sum_{\ell=0}^{\infty} \sum_{L=0}^{\infty} \chi_{\ell L}/R^{\ell+L+1} \quad . \qquad (14)$$

Therefore, from equations (13) and (1)

$$E(R) = R^{-2(\ell+L+1)} \langle\psi^o|U_{\ell L}|\chi_{\ell L}\rangle \qquad (15)$$

where $\chi_{\ell L}$ satisfies

$$[\mathcal{H}_o - E_o(I,II)]\chi_{\ell L} + [U_{\ell L} - \mathcal{E}^1(\ell,L)]\psi^o = 0 \qquad (16)$$

with $\mathcal{E}^1(\ell,L) = \langle\psi^o|U_{\ell L}|\psi^o\rangle$. For the reason stated earlier, $\mathcal{E}^1(\ell,L)$ is zero.

Equation (12) can be solved formally by expanding $\chi_{\ell L}$ in the complete set of unperturbed eigenfunctions of $\mathcal{H}_I$ and $\mathcal{H}_{II}$:[4]

$$\chi_{\ell L} = \sum_s \sum_t a_{st}(\ell,L)\varphi_I^s \phi_{II}^t \qquad (17)$$

where

$$(\mathcal{H}_I - E_I^s)\varphi_I^s = 0 \qquad (8b)$$

$$(\mathcal{H}_{II} - E_{II}^t)\,\phi_{II}^t = 0 \qquad (8c)$$

Substituting these into equation (13) and using equation (14), we obtain a representation for $a_{st}(\ell,L)$ which yields

$$\chi_{\ell L} = -\sum_s{}' \sum_t{}' \frac{\langle \varphi_I^o \phi_{II}^o | U_{\ell L} | \varphi_I^s \phi_{II}^t \rangle}{(E_I^s - E_I^o) + (E_{II}^t - E_{II}^o)} \varphi_I^s \phi_{II}^t \,. \qquad (18)$$

The primes on the summations indicate that the term s = t = o is to be omitted.

For neutral atoms in states with zero orbital angular momentum $E^2(I,II)$ is the primary contribution to the long-range interaction. Substituting equation (18) into the second order energy expression [equation (10) or (13)], we obtain

$$E^2(R) = -R^{-2(\ell+L+1)} \sum_s{}' \sum_t{}' \frac{|\langle \varphi_I^o \phi_{II}^o | U_{\ell L} | \varphi_I^s \phi_{II}^t \rangle|^2}{(E_I^s - E_I^o) + (E_{II}^t - E_{II}^o)} \,. \qquad (19)$$

Using the appropriate expression for $U_{\ell L}$ [equation (2)], we can arrive at the equation

$$E^2(R) = -16\pi^2 \sum_{\ell=1}^{\infty} \sum_{L=1}^{\infty} \frac{(2\ell+2L)!}{(2\ell+1)!(2L+1)!} R^{-2(\ell+L+1)}$$

$$\times \sum_{s}{}' \sum_{t}{}' \frac{|\langle \varphi_I^o | \sum_i r_i^{\ell} Y_\ell^o(\hat{r}_i) \varphi_I^s \rangle|^2 |\langle \phi_{II}^o | \sum_j r_j^{L} Y_L^o(\hat{\rho}_j) | \phi_{II}^t \rangle|^2}{(E_I^s - E_I^o) + (E_{II}^t - E_{II}^o)} \quad . \tag{20a}$$

This expression can be written in a more compact form as a sum over all the individual multipole interactions each times an appropriate inverse power of R:

$$E^2(R) = -\sum_{\ell=1}^{\infty} \sum_{L=1}^{\infty} \frac{C_2(\ell,L)}{R^{2(\ell+L+1)}} \tag{20b}$$

A. Methods for Calculating Long-Range Interactions

1. The Variational Method

It is not possible to solve equation (16) analytically, but for some systems a variational treatment can be employed successfully. The variational functional appropriate to equation (16) is[5]

$$\tilde{J}(\ell,L) = \langle \chi'_{\ell L} | \mathcal{H}_o - E_o(I,II) | \chi'_{\ell} \rangle + 2 \langle \chi'_{\ell L} | U_{\ell L} | \psi^o \rangle \tag{21}$$

where $\chi'_{\ell L}$ is some trial form of $\chi_{\ell L}$ containing variational parameters. The minimum value of equation (21) is $-C_2(\ell,L)$, the quantity we wish to obtain. The trial function usually has the form

$$\chi'_{\ell L} = \sum_i \sum_j F(r_i,\rho_j) \upsilon_{\ell L}(r_i,\rho_j) \psi^o \tag{22}$$

where $v_{\ell L}(r_i, \rho_j)$ is defined by

$$U_{\ell L} = \sum_i \sum_j v_{\ell L}(r_i, \rho_j)$$

although more elaborate functions have been used.

Variational calculations have been performed for interacting hydrogen atoms using various forms of the function $F(r_i \rho_j)$. Calculations of this type were first performed by Hassé (1930),[6] Slater and Kirkwood (1931),[7] and Pauling and Beach (1935).[8] The most precise values have been determined by Hirschfelder and Löwden (1959),[9] Davison (1966),[10] and Kolos (1967).[11] For more complex systems, the unperturbed wavefunction ψ^0 is not known, but certain approximations to it have been used. Davison used the 80-parameter Kinoshita representation of the helium wavefunction and obtained the most accurately calculated $c_2(\ell,L)$ values for H-He and He-He interactions.

Other variational procedures are available for the calculation of intermolecular forces. In particular, Sinanoglu and Kestner[12] have applied a two-center method using correlated wave functions to the He-He interaction. This method, as well as that of Brueckner and Goldstone (many body perturbation theory[13]) can be used for the more complex many electron systems, but thus far only small systems have been studied in a limited way.

2. The Semi-Empirical Method

Defining electric dipole oscillator strengths as

$$f_I^s = \frac{2}{3}(E_I^s - E_I^o)\,|\langle \varphi_I^o | \Sigma r_i | \varphi_I^s \rangle|^2 \qquad (24a)$$

$$f_{II}^t = \frac{2}{3}(E_{II}^t - E_{II}^o)\,|\langle \phi_{II}^o | \Sigma \rho_j | \phi_{II}^t \rangle|^2 \qquad (24b)$$

the leading term of equation (20) can be expressed in the form

$$\varepsilon_2(1,1) \approx -\frac{3}{2} \sum_s{}' \sum_t{}' f_I^s f_{II}^t \frac{[(E_I^s - E_I^o)(E_{II}^t - E_{II}^o)]^{-1}}{(E_I^s - E_I^o) + (E_{II}^t - E_{II}^o)} \quad . \qquad (25)$$

In this simple form, all available oscillator strengths, both from experimental and theoretical data, can be substituted into equation (25) to obtain $\varepsilon_2(1,1)$. The summations must include transitions to all bound as well as all continuum states. For most atoms, only a few of the required oscillator strengths are available. This lack of data can be circumvented by using the fact that oscillator strengths obey a series of sum rules.[14] These sum rules are equal or proportional to known quantities such as the polarizability, the refractive index, and the Verdet constant. The available set of oscillator strengths is augmented by selecting values for the remaining transitions in such a way that they satisfy the sum rules. The entire set can then be used to evaluate equation (25).

Equation (25) has been modified by Bell as an expansion containing only products of summations from centers I and II.[15] No oscillator strength distribution is required. Another modification by Dalgarno, Morrison, and Pengelly[16] proceeds directly from refractive

index data without using an oscillator-strength distribution or summations. Both of these approaches require extensive quantities of experimental data.

Observed optical transitions are almost always electric dipole allowed. Other types of electronic transitions due to higher multipole moments do not occur with sufficient intensity to be used as described above. For that reason, semi-empirical methods can only be applied effectively to dipole-dipole interactions. Nevertheless, these methods when properly applied do give the best currently available values for R^{-6} interactions and provide a useful check on the purely theoretical methods that are necessary to evaluate the higher terms in the series expansion of equation (20).

3. The One-Center Method

In the form of either equation (19) or (20) however, the calculation still involves a two-center problem. To obtain the one-center method, we make use of the following identity[17]

$$\frac{1}{a+b} = \frac{2}{\pi}\int_0^\infty \frac{ab}{(a^2+u^2)(b^2+u^2)}\,du \qquad . \qquad (24)$$

Using equation (26), equation (20) can be written as

$$E^2(R) = -16\pi^2 \sum_{\ell=1}^{\infty} \sum_{L=1}^{\infty} \frac{(2\ell+2L)!}{(2\ell+1)!(2L+1)!} R^{-2(\ell+L+1)}$$

$$X \frac{2}{\pi} \sum_s{}' \sum_t{}' \int_0^{\infty} \frac{(E_I^s-E_I^o)|W_{os}^{\ell}|^2(E_{II}^t-E_{II}^o)|W_{ot}^{L}|^2}{[(E_I^s-E_I^o)^2+u^2][(E_{II}^t-E_{II}^o)^2+u^2]} du \qquad (27)$$

using a notation which can be understood by referring back to equation (20).

The frequency dependent polarizability of an atom is given by[18]

$$\alpha_{\ell}(\nu) = \frac{8\pi}{2\ell+1} \sum_s{}' \frac{(E^s-E^o)|W_{os}^{\ell}|^2}{(E^s-E^o)^2-(h\nu)^2} . \qquad (28)$$

Introducing an imaginary frequency $u = ih\nu$, equation (28) becomes

$$\alpha_{\ell}(u) = \frac{8\pi}{2\ell+1} \sum_s{}' \frac{(E^s-E^o)|W_{os}^{\ell}|^2}{(E^s-E^o)^2+u^2} . \qquad (29)$$

Polarizabilities as a function of imaginary frequency are real. The use of equation (29) in equation (27) gives

$$E^2(R) = -\sum_{\ell=1}^{\infty} \sum_{L=1}^{\infty} \frac{(2\ell+2L)!}{4(2\ell)!(2L)!} R^{-2(\ell+L+1)} \frac{2}{\pi} \int_0^{\infty} \alpha_{\ell I}(u)\alpha_{LII}(u)du . \qquad (30)$$

The leading term is the common dipole-dipole interaction term,

$$\mathcal{E}^2(1,1) = -\frac{3}{\pi} \int_0^{\infty} \alpha_{1I}(u)\alpha_{1II}(u)du . \qquad (31)$$

From equation (30) we see that one needs to know only the polarizability of an atom as a function of imaginary frequencies in order to calculate the long-range induced multipole interactions. Equation (30) allows us to divorce ourselves completely from a two-center many-electron problem, even though we are intent upon calculating the long-range interactions of such a system.

In going from a two-center problem to a one-center one, we substituted for an atom-atom interaction two atom-electric field interactions. This substitution can be done because we are calculating long-range interactions with no electron cloud overlap and therefore can consider the interactions from the standpoint of induced multipole interactions.

Frequency dependent multipole polarizabilities were introduced in the form of equation (28) without any detailed derivation. Some of the necesssary background must now be presented. It is important to remember that we can limit our discussion to the polarizabilities of a single atom and need not be concerned with interactions of the more complex system of two atoms.

B. Atomic Polarizabilities

1. Definitions and Derivations

Atomic polarizabilities are a measure of the changes in the charge distribution of an atom when it interacts with an electric field.[19] When an atom is placed in a field, it is polarized and the resulting distribution of charge can be described by a series of induced electric

multipole moments, each of which is proportional to the external field. The induced dipole moment is related to the electric field by the atomic dipole polarizability, α_d.* The induced quadrupole moment is related to the gradient of the electric field by the atomic quadrupole polarizability, α_q. Similar relationships involving higher-order derivatives of the electric field apply to the higher pole polarizabilities.

In the case of an atom under the influence of a weak electric field, the interaction energy can be expressed in a power series of the electric field, F,

$$E = -\mu F - \tfrac{1}{2} \alpha F^2 + \ldots \quad . \quad (32)$$

Considering the external field to be a small perturbation, the perturbed energy can also be expressed in powers of the external field as

$$E = E^1 F + E^2 F^2 + \ldots \quad . \quad (33)$$

Comparing equations (32) and (33), we find

$$\alpha = -2E^2 \quad .$$

Thus, polarizability is proportional to certain terms in the energy when an external field is the perturbation.

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*Actually, the relation between the induced dipole moment and the electric field is a tensor relationship in which polarizability is a tensor, $\overleftrightarrow{\alpha}$. In the general case, the induced moment is not always parallel to the electric field. Since our atoms are spherically symmetric, we shall only be concerned with an isotropic tensor polarizability $\alpha_{xx} = \alpha_{yy} = \alpha_{zz} = \alpha$.

Consider a system described by a Hamiltonian $\mathcal{H}^{(o)}$, under the influence of a harmonic perturbation of the form[20]

$$\sim W = W(e^{i\omega^* t} + e^{-i\omega t}) \quad . \qquad (34)$$

W is assumed to be self-adjoint and ω^* is the complex conjugate of the frequency ω. These conditions insure that the perturbation is Hermitian. $\sim W$ is simply the time-dependent external field defined as F previously. The time-dependent Schrödinger equation for the perturbed system is then

$$i\dot{\Psi} = [\mathcal{H}^{(o)} + \lambda \sim W]\Psi \qquad (35)$$

where $\dot{\Psi}$ is simply $\partial\Psi/\partial t$, and t is time. Expanding Ψ in a power series in λ (an ordering parameter)

$$\Psi = \Psi^o + \lambda\psi^1 + \lambda^2\psi^2 + \ldots \quad , \qquad (36)$$

substituting equation (36) into (35), and equating terms of like powers in λ, we have

$$i\dot{\Psi}^o = \mathcal{H}^{(o)}\Psi^o \qquad (37)$$

$$i\dot{\Psi}^1 = \mathcal{H}^{(o)}\Psi^1 + \sim W\Psi^o \qquad (38)$$

$$i\dot{\Psi}^2 = \mathcal{H}^{(o)}\Psi^2 + \sim W\Psi^1 \qquad (39)$$

which are, respectively, the zero, first, and second order equations.

The solution to equation (37) is

$$\Psi^{o} = \Phi^{o} e^{-iE^{o}t} \qquad (40)$$

To solve equation (38), we write

$$\Psi^{1} = \psi_{-}^{1} e^{-i(E^{o}+\omega^{*})t} + \psi_{+}^{1} e^{-i(E^{o}-\omega)t} \qquad (41)$$

Substituting equations (34) and (41) into equation (38), we obtain two time-independent equations.

$$[\mathcal{H}^{(o)} - E^{o} - \omega]\psi_{-}^{1} + W\Phi^{o} = 0 \qquad (42)$$

$$[\mathcal{H}^{(o)} - E^{o} + \omega]\psi_{+}^{1} + W\Phi^{o} = 0 \qquad (43)$$

or

$$[\mathcal{H}^{(o)} - E^{o} \pm \omega]\psi_{\pm}^{1} + W\Phi^{o} = 0 \qquad (44)$$

Expanding the solutions of equation (44) in terms of eigenfunctions Φ^{s} of $\mathcal{H}^{(o)}$, we get

$$\psi_{\pm}^{1} = -\sum_{s}{}' \frac{\langle \Phi^{s} | W | \Phi^{o} \rangle}{E^{s} - E^{o} \pm \omega} \Phi^{s} \qquad (45)$$

The variational functional appropriate to equation (44) is

$$\tilde{L}_{\pm} = \langle \psi_{\pm}^{1} | \mathcal{H}^{(o)} - E^{o} \pm \omega | \psi_{\pm}^{1} \rangle + 2 \langle \psi_{\pm}^{1} | W | \Phi^{o} \rangle \qquad (46)$$

which gives optimal values[21] for these second-order properties which have the exact values

$$L_+ = \langle \psi_+^1 | W | \Phi^O \rangle \tag{47a}$$

and

$$L_- = \langle \psi_-^1 | W | \Phi^O \rangle \quad . \tag{47b}$$

The latter are obtained only if $\psi_\pm^1$ satisfy equation (44) exactly. The quantity of physical interest is usually the combination, $L = L_+ + L_-$,

$$L = -\Sigma_s' \frac{\langle \Phi^s | W | \Phi^O \rangle}{E^s - E^O + \omega} - \Sigma_s' \frac{\langle \Phi^s | W | \Phi^O \rangle^2}{E^s - E^O - \omega} \tag{47c}$$

which can be written as

$$L = -2\Sigma_s' \frac{(E^s - E^O)\langle \Phi^s | W | \Phi^O \rangle^2}{(E^s - E^O)^2 - \omega^2} \quad . \tag{48}$$

This is just the expression for a general time-dependent polarizability whenever W is of the proper form, and apart from a simple factor, is the same as equation (28).

2. Application to Long-Range Interactions

The frequency-dependent multipole polarizabilities in equation (48) or (28) describe the response of the atomic system to a time-varying electric field. If sufficient experimental data are available, these sums can be evaluated in the manner discussed in the previous section. However, this type of evaluation is limited to dipole polarizabilities, and so higher pole polarizabilities must be calculated theoretically.

Replacing ω in equation (48) with iu yields

$$\alpha_\ell(u) = -2\Sigma'_s \frac{(E^s-E^o)\,|\langle\Phi^s|W_\ell|\Phi^o\rangle|^2}{(E^s-E^o)^2+u^2} \tag{49}$$

where, for the 2^ℓ-pole polarizability, we must choose

$$W_\ell = -\Sigma_i r_i^\ell P_\ell(\cos\theta_i) = \Sigma_i w_i^{(\ell)} \ .$$

Equation (49) is the general expression for frequency-dependent polarizabilities for imaginary frequencies. Their calculation has prime importance if we are to obtain long-range interactions from equation (30). There are also advantages in working with $\alpha_\ell(u)$ as opposed to $\alpha_\ell(\omega)$. Not only are we allowed to use a simpler one-center method, but $\alpha_\ell(u)$ is a smooth function of u while $\alpha_\ell(\omega)$ has discontinuities (poles) at all excitations $[(E^s-E^o)-\omega]$ of the atom as can be seen from equation (48). A smooth function is easier to approximate than one containing singularities.

Equation (49) can be written in the following two ways[22] (see Appendix A):

$$\alpha_\ell(u) = 2\langle\Phi^o|W_\ell|\Theta\rangle \tag{51}$$

where Θ_ℓ is the solution to

$$[(H-E^o)^2+u^2]\Theta_\ell-\vec{\nabla}W_\ell\cdot\vec{\nabla}\,\Phi^o+\langle\Phi^o|\vec{\nabla}W_\ell\cdot\vec{\nabla}|\Phi^o\rangle\Phi^o-u^2\langle\Phi^o|\Theta_\ell\rangle\Phi^o = 0 \tag{52}$$

or, alternatively as

$$\alpha_\ell(u) = 2\langle\Phi^o|\vec{\nabla}W_\ell\cdot\vec{\nabla}|\Psi_\ell\rangle \qquad (53)$$

where Ψ_ℓ is the solution to

$$[(H-E^o)^2+u^2]\Psi_\ell - W_\ell\Phi^o - u^2\langle\Phi^o|\Psi_\ell\rangle\Phi^o = o \qquad (54)$$

Equations (52) and (54) can be solved by variational methods. Chan and Dalgarno[23] solved equation (54) for atomic hydrogen by minimizing the functional

$$\tilde{J}(u) = \langle\Psi_\ell|(H-E^o)^2+u^2|\Psi_\ell\rangle - 2\langle\Psi_\ell|W_\ell|\Phi^o\rangle - u^2\langle\Phi^o|\Psi_\ell\rangle^2 \qquad (55)$$

Using a trial function of the form

$$\Psi_\ell = \sum_{j=1}^{m} Y_j r^{j+\ell} P_\ell(\cos\theta)\Phi^o \qquad (56)$$

they obtained results for long-range forces comparable to the two-center calculations of Pauling and Beach,[8] Hirschfelder and Löwden,[9] and Davison.[10]

Another method of evaluating equation (49) for more complex systems is to begin with equation (47c).

$$\alpha_\ell(\omega) = -\Sigma'_s \frac{\langle\Phi^s|W_\ell|\Phi^o\rangle^2}{E^s-E^o+\omega} - \Sigma'_s \frac{\langle\Phi^s|W_\ell|\Phi^o\rangle^2}{E^s-E^o-\omega} \qquad (47c)$$

We then use the sum rule derived in Appendix A to obtain

$$\alpha_\ell(\omega) = -\langle\Phi^o|W_\ell|\psi_+^1\rangle - \langle\Phi^o|W_\ell|\psi_-^1\rangle \qquad (57)$$

where $\psi_\pm^1$ satisfy equation (57a)

$$(\mathcal{H}-E^o\pm\omega)\psi_\pm^1 - W_\ell\Phi^o \pm \omega\langle\psi_\pm^1|\Phi^o\rangle\Phi^o = 0 \qquad (57a)$$

This is an equation for real frequencies, and thus to calculate the terms in equation (30), we need to obtain values at imaginary frequencies. This can be done by obtaining analytical solutions to equation (57).[24] Suitable trial forms for $\psi_\pm^1$ have been constructed such that equations (57) or (48) can be represented by the form

$$\alpha_\ell(\omega) = \sum_{m=1} g_m/(V_m^2 - \omega^2) \qquad (58a)$$

Thus, equation (49) is approximated by

$$\alpha_\ell(u) = \sum_{m=1} g_m/(V_m^2 + u^2) \qquad (58b)$$

and the interaction coefficients from equation (30) now have the form

$$e_2(\ell,L) = -\frac{(2\ell+2L)!}{4(2\ell)!(2L)!}\sum_m\sum_{m'}\frac{g_m^I+g_{m'}^{II}}{V_m^I V_{m'}^{II}(V_m^I+V_{m'}^{II})} \qquad (59)$$

Equation (58a) is augmented with experimental data from oscillator strengths and refractive indices whenever suitable representations of Φ^o cannot be found.

For more complex many-electron atoms, appropriate eigenfunctions of the Hamiltonian, $\mathcal{H}^{(o)}$, cannot be found. It then becomes necessary to adopt the Hartree-Fock approximation as a description of the unperturbed atom. Since the Hartree-Fock Hamiltonian is not the exact Hamiltonian, we must consider this difference to be another perturbation. There are two perturbations acting on the Hartree-Fock atom. One perturbation is the difference between the exact and Hartree-Fock Hamiltonian of the free atom. This latter difference is usually denoted as V, and its effects are classified as electron correlation corrections since V now introduces the effects of the correlated motions of the electrons. In the Hartree-Fock approximation, the electrons move only in the average field of all of the other electrons. Since we have two perturbations, the effects of which are not mutually exclusive, we need to consider the methods of double perturbation theory as they apply to our particular problem.

C. General Formulation of Double Perturbation Theory for Many Electron Systems

Previously we developed the equations necessary to describe a system under the influence of a time-dependent harmonic perturbation. Expanding the first-order equations (42) and (43) in terms of the perturbation V, we have a new set of wavefunctions and a series expanded form for the Hamiltonian and the energy:

$$\mathcal{H}^{(o)} = \mathcal{H}^{(o,o)} + \mu V \tag{60}$$

$$\Phi^{o} = \psi^{(o,o)} + \mu\psi^{(1,o)} + \mu^{2}\psi^{(2,o)} + \ldots \tag{61}$$

$$E^{o} = E^{(o,o)} + \mu E^{(1,o)} + \mu^{2}E^{(2,o)} + \ldots \tag{62}$$

$$\psi_{\pm}^{1} = \psi_{\pm}^{(o,1)} + \mu\psi_{\pm}^{(1,1)} + \mu^{2}\psi_{\pm}^{(2,1)} + \ldots \tag{63}$$

where the first superscript indicates the order in the perturbation V, and the second superscript indicates the order in the external time-dependent perturbation. μ is simply an ordering parameter and can be set equal to unity whenever desired. Introducing these expansions into equations (42) and (43), we obtain from equation (43), for example,

$$[\mathcal{H}^{(o,o)} - E^{(o,o)} + \omega]\psi_{+}^{(o,1)} + W\psi^{(o,o)} = 0 \tag{64}$$

$$[\mathcal{H}^{(o,o)} - E^{(o,o)} + \omega]\psi_{+}^{(1,1)} + [V - E^{(1,o)}]\psi_{+}^{(o,1)} + W\psi^{(1,o)} = 0 \tag{65}$$

which are, respectively, the zero and first order equations for the perturbation V, correct to first order in the external perturbation W. From equation (42), we obtain similar equations for $\psi_{-}^{(o,1)}$ and $\psi_{-}^{(1,1)}$, but with ω replaced by $-\omega$.

1. Imaginary Frequencies

If ω is purely imaginary and $\omega = -iu$, then $\omega^{*} = iu$, and $\omega = -\omega^{*}$; whereas, if ω is real, we would have $\omega = \omega^{*}$. At imaginary frequencies

$$W = W(e^{-i\omega t} + e^{i\omega^{*}t}) = We^{-ut} \tag{66}$$

$$\Psi^{1} = [\psi_{+}^{1}e^{i\omega^{*}t} + \psi_{-}^{1}e^{-i\omega t}]e^{-iE^{o}t} = \psi^{1}e^{-(iE^{o}+u)t} \tag{67}$$

and

$$\Psi^2 = [\psi_o^2 + \psi_+^2 e^{2i\omega^* t} + \psi_-^2 e^{-2i\omega t}]e^{-iE^o t} = \psi^2 e^{-(E^o+2u)t} \quad . \quad (68)$$

Substituting these into the time-dependent first-order differential equation, equation (38), we obtain the following time-independent equation

$$[\{\mathcal{H}^{(o,o)} + \mu V\} - E^o + iu]\psi^1 + W\Phi^o = 0 \quad . \quad (69)$$

Expanding this in terms of the perturbation parameter μ, we get

$$[\mathcal{H}^{(o,o)} - E^{(o,o)} + iu)\psi^{(o,1)} + W\psi^{(o,o)} = 0 \quad (70)$$

and

$$[\mathcal{H}^{(o,o)} - E^{(o,o)} + iu]\psi^{(1,1)} + [V - E^{(1,o)}]\psi^{(o,1)} + W\psi^{(1,o)} = 0 \quad . \quad (71)$$

Expanding the wavefunctions $\psi^{(o,1)}$ and $\psi^{(1,1)}$ into real and imaginary parts as

$$\psi^{(o,1)} = \phi^{(o,1)} + i\theta^{(o,1)} \quad (72)$$

$$\psi^{(1,1)} = \phi^{(1,1)} + i\theta^{(1,1)} \quad (73)$$

and substituting into equations (70) and (71), we obtain the zero and first order real and imaginary equations.[25]

$$[\mathcal{H}^{(o,o)} - E^{(o,o)}]\phi^{(o,1)} - u\theta^{(o,1)} + W\psi^{(o,o)} = 0 \quad (74)$$

$$[\mathcal{H}^{(o,o)} - E^{(o,o)}]\theta^{(o,1)} + u\phi^{(o,1)} = 0 \quad (75)$$

$$[\mathcal{H}^{(o,o)} - E^{(o,o)}]\phi^{(1,1)} - u\theta^{(1,1)} + [V - E^{(1,o)}]\phi^{(o,1)} + W\psi^{(1,o)} = 0 \quad (76)$$

$$[\mathcal{H}^{(o,o)} - E^{(o,o)}]\theta^{(1,1)} + u\phi^{(1,1)} + [V - E^{(1,o)}]\theta^{(o,1)} = 0 \quad (77)$$

2. Polarizability Equations

Polarizabilities correct to first order in electron correlation are

$$-\tfrac{1}{2}\alpha(u)e^{-2ut} = \langle \Psi^{1*} | \mathcal{W} | \Psi^{o} \rangle \tag{78}$$

$$= \langle [\psi^{(o,1)} + \mu\psi^{(1,1)}] e^{(iE^{o}-u)t} | We^{-ut} | [\psi^{(o,o)} + \mu\psi^{(1,o)}] e^{-iE^{o}t} \rangle$$

$$= [\langle \psi^{(o,1)} | W | \psi^{(o,o)} \rangle + \mu \langle \psi^{(o,1)} | W | \psi^{(1,o)} \rangle + \mu \langle \psi^{(1,1)} | W | \psi^{(o,o)} \rangle] e^{-2ut}$$

$$= [\langle \phi^{(o,1)} | W | \psi^{(o,o)} \rangle + \mu \langle \phi^{(o,1)} | W | \psi^{(1,o)} \rangle + \mu \langle \phi^{(1,1)} | W | \psi^{(o,o)} \rangle] e^{-2ut} \tag{79}$$

if the external field has an amplitude of unity. The particular polarizability calculated depends on the form of W, i.e., which W_{ℓ}. In equation (79), $\phi^{(1,1)}$ and $\psi^{(1,o)}$ are wavefunctions including correlation. These wavefunctions are difficult to determine for many electron systems. Equation (79) can be simplified with the use of equations (70) and (71). From these two equations we obtain

$$\langle \psi^{(1,1)} | W | \psi^{(o,o)} \rangle = \langle \psi^{(o,1)} | V\text{-}E^{(1,o)} | \psi^{(o,1)} \rangle + \langle \psi^{(o,1)} | W | \psi^{(1,o)} \rangle . \tag{80}$$

Using equations (72) and (73) in equation (80), we obtain the more useful form:

$$\langle \phi^{(1,1)} | W | \psi^{(o,o)} \rangle = \langle \phi^{(o,1)} | V\text{-}E^{(1,o)} | \phi^{(o,1)} \rangle - \langle \theta^{(o,1)} | V\text{-}E^{(1,o)} | \theta^{(o,1)} \rangle + \langle \phi^{(o,1)} | W | \psi^{(1,o)} \rangle \tag{81}$$

which, when substituted into equation (79), yields

$$-\tfrac{1}{2}\alpha(u) = \langle\phi^{(0,1)}|W|\psi^{(0,0)}\rangle + \mu\,[\langle\phi^{(0,1)}|V-E^{(1,0)}|\phi^{(0,1)}\rangle$$

$$+ 2\,\langle\phi^{(0,1)}|W|\psi^{(1,0)}\rangle - \langle\theta^{(0,1)}|V-E^{(1,0)}|\theta^{(0,1)}\rangle]\,. \quad (82)$$

Only in the term, $2\langle\phi^{(0,1)}|W|\psi^{(1,0)}\rangle$, is there involved a correlated wave function. This can be eliminated by defining a function of second order in the external perturbation. Define $\psi^{(0,2)}$ by[21]

$$[\mathcal{H}^{(0,0)}-E^{(0,0)}]\psi^{(0,2)} = -W\phi^{(0,1)} + \langle\psi^{(0,0)}|W|\phi^{(0,1)}\rangle\psi^{(0,0)}\,. \quad (83)$$

Then, upon multiplying this equation by $\psi^{(1,0)}$ and integrating, we obtain

$$\langle\psi^{(1,0)}|[\mathcal{H}^{(0,0)}-E^{(0,0)}]|\psi^{(0,2)}\rangle = -\langle\psi^{(1,0)}|W|\phi^{(0,1)}\rangle \quad (84)$$

since $\langle\psi^{(1,0)}|\psi^{(0,0)}\rangle = 0$.

From equations (37), (60), and (61), we have

$$[\mathcal{H}^{(0,0)}-E^{(0,0)}]\psi^{(0,0)} = 0 \quad (85)$$

and

$$[\mathcal{H}^{(0,0)}-E^{(0,0)}]\psi^{(1,0)} + [V-E^{(1,0)}]\psi^{(0,0)} = 0\,. \quad (86)$$

Multiplying equation (86) by $\psi^{(0,2)}$ and integrating, we find after comparing this result with equation (84), that

$$\langle\phi^{(0,1)}|W|\psi^{(1,0)}\rangle = \langle\psi^{(0,0)}|V-E^{(1,0)}|\psi^{(0,2)}\rangle\,. \quad (87)$$

Substituting equation (87) into (82), we have a result which is easily evaluated.

$$-\tfrac{1}{3}\alpha(u) = \langle \phi^{(o,1)} | W | \psi^{(o,o)} \rangle + \mu \left[\langle \phi^{(o,1)} | V-E^{(o,1)} | \phi^{(o,1)} \rangle \right.$$

$$\left. - \langle \theta^{(o,1)} | V-E^{(o,1)} | \theta^{(o,1)} \rangle + 2 \langle \psi^{(o,o)} | V-E^{(1,o)} | \psi^{(o,2)} \rangle \right] \quad (88)$$

or

$$\alpha(u) = \alpha^{o}(u) + \alpha^{1}(u) \quad (89)$$

Equation (88) expresses frequency dependent polarizabilities correct to first order in electron correlation without using any correlated atomic wavefunctions. Any particular $\alpha_{\ell}(u)$ can be calculated if the appropriate choice for W_{ℓ} is made. We retain μ in equation (88) only to designate all terms which depend on V to the first power.

D. Zero Order Hamiltonian and Trial Functions

There are essentially two types of Hartree-Fock methods used in atomic calculations.[28] If perturbed orbitals are forced to be completely independent of each other, we have the uncoupled procedure. When the orbitals are not restricted to perturb independently, the coupled version results. We will make use of the uncoupled approximation in our calculations, as this is the simpler form and previous work indicates it can achieve comparable accuracy.[27]

From uncoupled Hartree-Fock theory, we know the forms of $\psi^{(o,o)}$, $\phi^{(o,1)}$, and $\psi^{(o,2)}$.[28] These are

$$\psi^{(o,o)} = A \prod_{i} \varphi_i^{o}(i) \quad (90)$$

$$\phi^{(o,1)} = \sum_{j} A \prod_{i \neq j} [\varphi_i^{o}(i) \varphi_j^{1}(j)] \quad (91)$$

$$\theta^{(o,1)} = u\Sigma A \prod_{i\ i\neq j} [\theta_i^o(i)\theta_j^1(j)] \tag{92}$$

$$\psi^{(o,2)} = \Sigma A \prod_{k\ i\neq k} [\varphi_i^o(i)\varphi_k^2(k) + u^2\theta_i^o\theta_k^2(k)]$$

$$+ \Sigma A \prod_{k<\ell\ i\neq k,\ell} [\varphi_i^o(i)\varphi_k^1(k)\varphi_\ell^1(\ell) + u^2\theta_i^o(i)\theta_k^1(k)\theta_\ell^1(\ell)] \tag{93}$$

where A is the normalized antisymmetrizer,[29] $\varphi_i^o(i)$ is the unperturbed Hartree-Fock spin orbital satisfying the equation,

$$(h_i^o - \mathcal{E}_i^o)\varphi_i^o(i) = 0 \tag{94}$$

and $\varphi_j^1(j)$ is the uncoupled Hartree-Fock approximation to the first order perturbed wavefunction. The products and summations include all of the n electrons in the atom.

We define our zero-order one-electron Hartree-Fock Hamiltonian as

$$h_i^o = -\tfrac{1}{2}\nabla_i^2 - \frac{Z}{r_i} + \sum_{i\neq j} [J_j(i) - K_j(i)] \tag{95}$$

where

$$J_j(i) = \langle\varphi_j^o(j)|\frac{1}{r_{ij}}|\varphi_j^o(j)\rangle_j \tag{96a}$$

$$K_j(i) = \langle\varphi_j^o(j)|\frac{1}{r_{ij}}|\varphi_i^o(j)\rangle_j \tag{96b}$$

which are known as the coulomb and exchange operators respectively.[29] $K_j(i)$ is zero if orbitals i and j have different spins. The integration is performed over coordinates of electron j.

The above definition of h_i^o is different from the usual Hartree-Fock in that the self-interaction terms, those involving i = j, have been omitted. Doing this does not alter the zero-order equation, and experience has shown that including these terms, which are an artifact of the Hartree-Fock procedure, yields results which are invariably less accurate.[27]

The total (non-relativistic) Hamiltonian of an atom in an electric field is (in atomic units)

$$\mathcal{H} = \sum_i -\tfrac{1}{2}\nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_{i<j} \frac{1}{r_{ij}} + \mathcal{W} = \mathcal{H}^{(o,o)} + V + \mathcal{W} \quad . \quad (97)$$

The Hartree-Fock Hamiltonian is

$$\mathcal{H} = \sum_i h_i^o = \sum_i -\tfrac{1}{2}\nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_{i\neq j} [J_j(i) - K_j(i)] \quad . \quad (98)$$

From equations (97) and (98) we find

$$V = \sum_{i<j} \frac{1}{r_{ij}} - \sum_{i\neq j} [J_j(i) - K_j(i)] \quad . \quad (99)$$

Zero-order Hartree-Fock wavefunctions φ_i^o are well known and can be easily obtained from the literature.[30] Perturbed wavefunctions $\phi^{(o,1)}$, $\theta^{(o,1)}$, and $\psi^{(o,2)}$ must be calculated for the particular problem from the appropriate differential equations. We see from equation (93) that one electron excitation terms, φ^1 and θ^1, in $\psi^{(o,2)}$ are completely determined by the one-electron excitation terms in $\phi^{(o,1)}$ and $\theta^{(o,1)}$.

The last term in equation (88), $2\langle\psi^{(o,o)}|V-E^{(1,o)}|\psi^{(o,2)}\rangle$, is the first-order electron correlation contribution of $\psi^{(o,2)}$ to the polarizability. If $\psi^{(o,o)}$ is a closed shell Hartree-Fock wavefunction, the contribution of singly excited configurations involving the φ_k^2 and the θ_k^2 vanishes by Brillouin's Theorem.[21] Therefore, to calculate

polarizabilities correct to first-order in electron correlation [equation (88)], we need to calculate only $\phi^{(0,1)}$ and $\theta^{(0,1)}$ because the contributions from $\psi^{(0,2)}$ can be completely determined if $\phi^{(0,1)}$ and $\theta^{(0,1)}$ are known. Furthermore, it is shown in Appendix C that the $\theta^{(0,1)}$ term in equation (88) does not contribute to the polarizability if equation (99) is used as our Hartree-Fock potential.

Combining equations (74) and (75), we find

$$[\{\mathcal{H}^{(0,0)}-E^{(0,0)}\}^2+u^2]\phi^{(0,1)} + [\mathcal{H}^{(0,0)}-E^{(0,0)}]W\psi^{(0,0)} = 0 \quad (100)$$

which can be solved variationally by minimizing the following functional

$$\tilde{J}(\phi) = \langle\phi^{(0,1)}|[\mathcal{H}^{(0,0)}-E^{(0,0)}]^2+u^2|\phi^{(0,1)}\rangle + 2\langle\phi^{(0,1)}|[\mathcal{H}^{(0,0)}-E^{(0,0)}]W|\psi^{(0,0)}\rangle \quad (101)$$

with respect to trial forms of $\phi^{(0,1)}$. In our calculations, we used the following trial function.

$$\phi^{(0,1)} = \sum_{i=1}^{m}\sum_{j=1}^{m} Y_{ij}^{(\ell)} r_i^{\ell} P_{\ell}(\cos\theta_i)\psi^{(0,0)} = \sum_{i}^{m}\sum_{j}^{m} \mathcal{F}_{ij}^{(\ell)}(r_{ij}\theta_i)\psi^{(0,0)} \quad (102)$$

The value of m is selected large enough to achieve convergence of all functionals. This trial function is of the form shown to be exact in static polarizability calculations of atomic hydrogen and has been used successfully in a wide variety of similar calculations.[31] The perturbed states must be orthogonal to ground states, thus we Schmidt orthogonalize each $\phi^{(0,1)}$ to yield the actual trial function.

$$\mathcal{P}^{(o,1)} = \phi^{(o,1)} - \langle \phi^{(o,1)}, \psi^{(o,o)} \rangle \psi^{(o,o)} \quad . \qquad (103)$$

Putting all of these equations together, the functional to be solved for each electron i is

$$\begin{aligned}
\tilde{J}_i[\phi^{(o,1)}] = \sum_{j,k=1}^{m} [& \langle \mathcal{F}_{ij}^{(\ell)} \varphi_i^o | (h_i^o - \varepsilon_i^o)^2 + u^2 | \mathcal{F}_{ik}^{(\ell)} \varphi_i^o \rangle \\
& - \sum_n \langle \mathcal{F}_{ij}^{(\ell)} \varphi_i^o | (h_i^o - \varepsilon_i^o)^2 + u^2 | \varphi_n^o \rangle \langle \mathcal{F}_{ik}^{(\ell)} \varphi_i^o | \varphi_n^o \rangle \\
& - \sum_n \langle \varphi_n^o | (h_i^o - \varepsilon_i^o)^2 + u^2 | \mathcal{F}_{ik}^{(\ell)} \varphi_i^o \rangle \langle \mathcal{F}_{ij}^{(\ell)} \varphi_i^o | \varphi_n^o \rangle \\
& + \sum_n \langle \varphi_n^o | (h_i^o - \varepsilon_i^o)^2 + u^2 | \varphi_n^o \rangle \langle \mathcal{F}_{ij}^{(\ell)} \varphi_i^o | \varphi_n^o \rangle \langle \mathcal{F}_{ik}^{(\ell)} \varphi_i^o | \varphi_n^o \rangle \\
& + 2 \langle \mathcal{F}_{ij}^{(\ell)} \varphi_i^o | (h_i^o - \varepsilon_i^o) W_\ell | \varphi_i^o \rangle \\
& - 2 \sum_n \langle \mathcal{F}_{ij}^{(\ell)} \varphi_i^o | \varphi_n^o \rangle \langle \varphi_n^o | (h_i^o - \varepsilon_i^o) W_\ell | \varphi_i^o \rangle] \quad . \qquad (104)
\end{aligned}$$

The sum over n includes all occupied Hartree-Fock orbitals. Since the only variable parameter in $\mathcal{F}_{ij}^{(\ell)}$ is the coefficients $Y_{ij}^{(\ell)}$, the condition that $\delta \tilde{J}_i[\phi^{(o,1)}] = 0$ is equivalent to requiring $\partial \tilde{J}[\phi^{(o,1)}/\partial Y_{ij} = 0$ or

$$\partial \tilde{J}_i[\phi^{(o,1)}]/\partial Y_{ij}^{(\ell)} = 2 \sum_{k=1}^{m} Y_{ik}^{(\ell)} B_{jk}^{(\ell)} + 2 C_j^{(\ell)} = 0 \text{ for all } j = 1,m \; . \quad (105)$$

We thus have to solve an mxm matrix equation to obtain the mY_{ij} coefficients for each electron i. From equation (104), B_{jk} and C_j in

equation (105) are

$$B^{(\ell)}_{jk} = \langle f^{(\ell)}_{ij}\varphi^o_i|(h^o_i-\varepsilon^o_i)^2+u^2|f^{(\ell)}_{ik}\varphi^o_i\rangle$$

$$- \sum_n \langle f^{(\ell)}_{ij}\varphi^o_i|(h^o_i-\varepsilon^o_i)^2+u^2|\varphi^o_n\rangle\langle f^{(\ell)}_{ik}\varphi^o_i|\varphi^o_n\rangle$$

$$- \sum_n \langle \varphi^o_n|(h^o_i-\varepsilon^o_i)^2+u^2|f^{(\ell)}_{ik}\varphi^o_i\rangle\langle f^{(\ell)}_{ik}\varphi^o_i|\varphi^o_n\rangle$$

$$+ \sum_n \langle \varphi^o_n|(h^o_i-\varepsilon^o_i)^2+u^2|\varphi^o_n\rangle\langle f^{(\ell)}_{ij}\varphi^o_n\rangle\langle f^{(\ell)}_{ik}\varphi^o_i|\varphi^o_n\rangle \qquad (106)$$

$$C^{(\ell)}_j = \langle f^{(\ell)}_{ij}\varphi^o_i|(h^o_i-\varepsilon^o_i)W_\ell|\varphi^o_i\rangle - \sum_n \langle f^{(\ell)}_{ij}\varphi^o_i|\varphi^o_n\rangle\langle\varphi^o_n|(h^o_i-\varepsilon^o_i)W_\ell|\varphi^o_i\rangle \qquad (107)$$

where

$$f^{(\ell)}_{ij} = r^j_i P_\ell(\cos\theta) \quad . \qquad (108)$$

When equation (106) is expanded, the most difficult term that arises is $\langle f^{(\ell)}_{ij}\varphi^o_i|(h^o_i-\varepsilon^o_i)^2|f^{(\ell)}_{ik}\varphi^o_i\rangle$. This can be written as

$$\langle(h^o_i-\varepsilon^o_i)f^{(\ell)}_{ij}\varphi^o_i|(h^o_i-\varepsilon^o_i)f^{(\ell)}_{ik}\varphi^o_i\rangle = \langle[-\tfrac{1}{2}\nabla^2_i, f^{(\ell)}_{ij}]\varphi^o_i|[-\tfrac{1}{2}\nabla^2_i, f^{(\ell)}_{ik}]\varphi^o_i\rangle \qquad (109)$$

where we have assumed that all but the $-\frac{1}{2}\nabla^2_i$ term in h^o_i has commuted with $f^{(\ell)}_{ij}$. This assumption could be removed by writing V in a form which totally commutes with $f^{(\ell)}_{ij}$. The difference in the two methods would be small because there is only a small exchange term involved in this approximation. For two electron systems, the commutation and resulting

equations are rigorously correct. It is only in larger systems that a very small error is introduced by equation (109). Our final results will completely justify the merits and accuracy of this assumption.

If φ_i^o is written as a product of an angular and a radial part, i.e., as $\varphi_i^o = Y_{\ell m}\varphi_i^o(r)$, then it can be shown that (see Appendix B)

$$[-\tfrac{1}{2}\nabla_i^2, f_{ij}^{(\ell)}]\varphi_i^o = -\tfrac{1}{2}(\nabla_i^2 F_{ij}^{(\ell)})\varphi_i^o(r) - \frac{\ell(\ell+1)}{2r^2} F_{ij}^{(\ell)}\varphi_i^o(r)$$

$$- \nabla_r F_{ij}^{(\ell)} \cdot \vec{\nabla}\varphi_i^o(r) \qquad (110)$$

where

$$F_{ij}^{(\ell)} = f_{ij}^{(\ell)} Y_{\ell m} \quad . \qquad (111)$$

The different $F_{ij}^{(\ell)}$ expressions can be found in Appendix B, along with the general terms for $B_{jk}^{(\ell)}$ and $C_j^{(\ell)}$ for each orbital. From equation (105), we obtain the coefficients for all terms in $\mathcal{H}^{(o,1)}$. Substituting these into equation (88), we can obtain polarizabilities correct to first-order in electron correlation. If we write

$$D_{ij}^{(\ell)} = \langle r_i^j P_\ell(\cos\theta_i)\varphi_i^o - \sum_k \langle r_i^j P_\ell(\cos\theta_i)\varphi_k^o\rangle \varphi_i^o | W_i^{(\ell)}\varphi_i^o\rangle \qquad (112)$$

then the zero-order term in equation (88) can be written as

$$\alpha_\ell^o(u) = -2 \sum_{i=1}^{n} \sum_{j=1}^{m} Y_{ij}^{(\ell)} D_{ij}^{(\ell)} \quad . \qquad (113)$$

The first-order correction terms in equation (88) are not as simple and

are especially difficult for large atoms. To solve these correction terms, we need expressions for both V and $E^{(1,0)}$. For V we use equation (99). From equation (86),

$$E^{(1,0)} = \langle \psi^{(0,0)} | V | \psi^{(0,0)} \rangle \quad . \tag{114}$$

Substituting equation (99) into equation (114), we have the standard result

$$E^{(1,0)} = \sum_{i<j} \langle \varphi_i^0(i)\varphi_j^0(j) | \frac{1}{r_{ij}}(1-P_{ij}) | \varphi_i^0(i)\varphi_j^0(j) \rangle \tag{115}$$

where P_{ij} is the permutation operator for electrons i and j. From equations (99) and (115), and using equations (90)-(93), we find (see Appendix C)

$$\alpha^1(u) = 4 \sum_{i<j} \langle \varphi_i^1(i)\varphi_j^0(j) | (1-P_{ij})\frac{1}{r_{ij}} | \varphi_i^0(i)\varphi_j^1(j) \rangle \quad . \tag{116}$$

III. RESULTS AND DISCUSSION

A. Two Electron Atoms

The essential results of this Section have been published, and a reprint is included in Appendix D; therefore, only a limited discussion is presented here.

Whenever a general method is to be developed to calculate some property or properties of an atom or system of atoms, one usually has to develop the equations for the simplest appropriate system and then expand the method to more complicated systems. Calculations for helium and other two electron ^1S state atoms presented no special problems when our method was used to calculate polarizabilities. Correlation corrections were relatively easy to calculate, because only two electrons are involved and the exchange operator is not present. The commutation relation [equation (109)] used in the calculations is no longer an assumption for two electron atoms, as it is rigorously correct. Thus, the accuracy for two electron system depends formally upon the use of the uncoupled Hartree-Fock method rather than the fully coupled theory. Also, perturbation theory is less accurate whenever the perturbation, in our case the electron correlation correction, is not small. The uncoupled method is inherently less accurate, but it is much easier to apply, requires much less computation time, and for larger systems is the more expedient method. Moreover, even the coupled method is not exact.

Table I presents a comparison of several methods of obtaining helium atom polarizabilities at zero frequencies. Of interest in this

Table I

Comparison of Several Methods of Obtaining Helium Atom Polarizabilities at Zero Frequency

Method	Dipole polarizability (in units of a_o^3)	Quadrupole polarizability (in units of a_o^5)
Method c(Epstein and Johnson)[a]	1.242	2.210
Geometric extrapolation of Method c[b]	1.319	2.329
This paper	1.294	2.326
Geometric extrapolation of this paper's results[b]	1.316	2.326
Coupled perturbation Theory[c]	1.323	2.331
Exact[d]	1.380	2.440

[a] S. Epstein and R. E. Johnson, J. Chem. Phys. 47, 2275 (1967).

[b] The geometric approximation is discussed in Ref. 32 in the text. It is equivalent to a [10] Padé approximant.

[c] P. W. Langhoff, M. Karplus, and R. P. Hurst, J. Chem. Phys. 44, 505 (1966).

[d] W. D. Davison, Proc. Phys. Soc. (London) 87, 133 (1966).

table is the use of a geometric approximation.[32] The geometric approximation assumes that the series

$$\alpha_\ell(0) = \alpha_\ell^o(0) + \Delta\alpha$$

are the first terms in the more general result

$$\alpha_\ell^{geom}(0) = \frac{\alpha_\ell^o(0)}{1-[\Delta\alpha/\alpha_\ell^o(0)]} \quad .$$

We find that the geometric approximation applied to the different uncoupled results yields values which agree with one another and more interestingly it causes them to agree with the more accurate coupled result. The geometric approximation then provides us with a simplified method of checking our uncoupled results with other more accurate calculations.

B. Ten Electron Atoms

1. Polarizabilities

The numerical results for this Section are presented in Tables II through XXIII. The results for Ne and Na^+ are the most important, because the more highly ionized species tend to be less polarized and have smaller dispersion interactions due to the increased nuclear charge on each center. In Figure 1, we have shown a linear relationship between each multipole polarizability and some inverse

Table II

Comparison of Several Methods of Obtaining Static Polarizabilities

		This paper	Uncoupled H-F Method	$\alpha^{a}_{geom.}$	$\alpha^{b}_{geom.}$	Coupled H-F Method
Ne	Dipole[h]	2.255	2.18[c] 2.84[d]	2.36	2.37	2.362[e] 2.361[f] 2.382[g]
	Quadrupole	4.822	6.32[d]	5.16	----	6.46[f]
	Octupole	34.533	35.33[d]	34.57	----	----
Na^{+}	Dipole	0.916	0.900[c] 1.112[d]	0.962	0.950	0.945[e] 0.945[f]
	Quadrupole	1.264	1.539[d]	1.33	----	1.524[f]
	Octupole	4.541	4.760[d]	4.55	----	----
Mg^{2+}	Dipole	0.460	0.453[c]	0.481	0.473	0.471[e] 0.470[f]
	Quadrupole	0.452	0.527[d]	0.460	----	0.518[f]
	Octupole	1.007	1.060[d]	1.01	----	----
Al^{3+}	Dipole	0.261	0.256[c]	0.266	0.267	0.268[e] 0.265[f]
	Quadrupole	0.193	0.219[d]	0.195	----	0.216[f]
	Octupole	0.298	0.314[d]	0.298	----	----

[a] Geometric approximation of this paper's results.

[b] Extrapolation of results from reference c

[c] D. F. Tuan and K. K. Wu, J. Chem. Phys. 53, 620 (1970). This includes first-order corrections.

[d] P. W. Langhoff and R. P. Hurst, Phys. Rev. 139, A1415 (1965). Zero-order only.

[e] H. D. Cohen, J. Chem. Phys. 45, 10 (1966).

[f] J. Lahire and A. Mukherji, Phys. Rev. 153, 386 (1960).

[g] V. G. Kaveeshwar, K. T. Chung, and R. P. Hurst, Phys. Rev. 172, 35 (1968).

[h] The exact value is estimated to be 2.663. A. Dalgarno and A. E. Kingston, Proc. Roy. Soc. 259A, 424 (1960).

Table III

Comparison of C_6 Interaction

Atoms	This paper	Semiempirical		Uncoupled Hartree-Fock
Ne-Ne	7.752[a]	6.63[c]	6.31[d]	7.57[g]
	5.097[b]	6.42[e]	6.38[f]	

[a] Without correlation

[b] With Correlation

[c] A. Dalgarno and A. E. Kingston, Proc. Phys. Soc. 259A, 422 (1961).

[d] A. E. Kingston, Phys. Rev. 135, A1018 (1964).

[e] J. A. Barker and P. J. Leonard, Phys. Letters 13, 127 (1964).

[f] R. J. Bell, Proc. Phys. Soc. (London) 86, 17 and 239 (1965).

[g] M. Karplus and H. J. Kolker, J. Chem. Phys., 41, 3955 (1964).

Table IV

Static polarizabilities for Ne isoelectronic sequence

Atom	Dipole		Quadrupole		Octupole	
	No Correlation	With Correlation	No Correlation	With Correlation	No Correlation	With Correlation
Ne	2.9009[a]	2.2403[a]	6.302[a]	4.668[a]	33.052[a]	31.898[a]
	2.9155[b]	2.2550[b]	6.482[b]	4.822[b]	35.682[b]	34.533[b]
Na^{+}	1.1257[a]	0.9135[a]	1.5293[a]	1.2589[a]	4.564[a]	4.4274[a]
	1.1298[b]	0.9160[b]	1.5369[b]	1.2640[b]	4.681[b]	4.5411[b]
Mg^{2+}[b]	0.5506	0.4596	0.5221	0.4515	1.034	1.007
Al^{3+}[b]	0.3061	0.2607	0.2166	0.1930	0.3050	0.2980
Si^{4+}[b]	0.1856	0.1605	0.1024	0.0930	0.1086	0.1064

[a]Hartree-Fock orbitals from, P. Bagus and T. L. Gilbert, Argonne National Laboratory (unpublished work).

[b]Hartree-Fock orbitals from, E. Clementi, IBM, J. Res. Develop., 9, 2 (1965).

Table V

Dispersion interactions for Ne isoelectronic sequence

Atoms	C_6		C_8		C_{10}[a]			
					C_{qq}		C_{do}	
	No Correlation	With Correlation	No Correlation	With Correlation	No Correlation	With Correlation	No Correlation	With Correlation
Ne-Ne[b]	7.727	5.074	87.03	58.66	457.93	317.99	836.52	661.30
Ne-Ne[c]	7.752	5.097	88.47	59.72	471.45	327.85	881.27	697.38
Na^+-Na^+[b]	2.023	1.444	14.43	10.76	48.17	37.54	79.07	65.53
Na^+-Na^+[c]	2.029	1.446	14.46	10.77	48.21	37.53	80.33	66.50
Mg^{2+}-Mg^{2+}[c]	0.721	0.540	3.618	2.843	8.50	7.01	13.17	11.22
Al^{3+}-Al^{3+}[c]	0.307	0.238	1.155	0.940	2.04	1.74	3.01	2.61
Si^{4+}-Si^{4+}[c]	0.147	0.117	0.433	0.362	0.598	0.523	0.854	0.753

[a] C_{qq} is the quadrupole-quadrupole contribution while C_{do} is the dipole-octupole contribution.

[b] Orbitals from P. Bagus and T. L. Gilbert (unpublished work).

[c] Orbitals from E. Clementi, IBM, J. Res. Develop., 9, 2 (1965).

Table VI

Dipole polarizabilities of Neon at imaginary frequencies (in atomic units) $\alpha_\ell(u)$[a]

u	$1s \rightarrow p$	$2s \rightarrow p$	$2p_{\pm1} \rightarrow d_{\pm1}$	$2p_o \rightarrow d_o$	$2p_o \rightarrow s$	$\alpha_1^o(u)$	$\alpha_1^o(u)+\alpha_1^1(u)$
0.0	0.0011	0.0468	1.2824	0.8550	0.7156	2.901	2.240
0.10	0.0011	0.0468	1.2740	0.8493	0.7032	2.874	2.222
0.30	0.0011	0.0462	1.2114	0.8076	0.6186	2.685	2.091
0.50	0.0011	0.0452	1.1075	0.7383	0.5023	2.394	1.888
0.80	0.0011	0.0429	0.9278	0.6185	0.3504	1.941	1.566
1.00	0.0011	0.0410	0.8147	0.5431	0.2767	1.677	1.374
1.50	0.0011	0.0360	0.5881	0.3921	0.1633	1.181	1.002
2.00	0.0011	0.0311	0.4346	0.2898	0.1056	0.8621	0.7524
2.50	0.0011	0.0268	0.3309	0.2206	0.0735	0.6528	0.5821
3.00	0.0011	0.0231	0.2589	0.1726	0.0541	0.5098	0.4623
4.00	0.0010	0.0175	0.1698	0.1132	0.0329	0.3344	0.3106
5.00	0.0010	0.0136	0.1192	0.0795	0.0223	0.2356	0.2224
6.00	0.0010	0.0108	0.0880	0.0587	0.0162	0.1747	0.1668
7.00	0.0010	0.0088	0.0675	0.0450	0.0124	0.1346	0.1296
8.00	0.0010	0.0073	0.0533	0.0355	0.0098	0.1069	0.1035
9.00	0.0010	0.0062	0.0431	0.0287	0.0080	0.0869	0.0846
10.00	0.0010	0.0053	0.0356	0.0237	0.0066	0.0721	0.0704

[a]Orbitals from P. Bagus and T. L. Gilbert, Argonne National Laboratory (unpublished work).

Table VII

Quadrupole polarizabilities of Neon at imaginary frequencies (in atomic units) $\alpha_\ell(u)$[a]

u	$1s \rightarrow d$	$2s \rightarrow d$	$2p_{\pm1} \rightarrow p_{\pm1}$	$2p_{\pm1} \rightarrow f_{\pm1}$	$2p_o \rightarrow p_o$	$2p_o \rightarrow f_o$	$\alpha_2^o(u)$	$\alpha_2^o(u) + \alpha_2^1(u)$
0.0	0.0	0.5939	0.8263	1.8455	1.6525	1.3841	6.302	4.668
0.10	0.0	0.5928	0.8152	1.8364	1.6305	1.3773	6.252	4.651
0.30	0.0	0.5837	0.7373	1.7680	1.4746	1.3260	5.890	4.517
0.50	0.0	0.5665	0.6212	1.6490	1.2425	1.2368	5.316	4.256
0.80	0.0	0.5290	0.4537	1.4282	0.9074	1.0712	4.390	3.720
1.00	0.0	0.4990	0.3657	1.2794	0.7315	0.9596	3.835	3.342
1.50	0.0	0.4186	0.2220	0.9597	0.4441	0.7198	2.764	2.515
2.00	0.0	0.3438	0.1450	0.7270	0.2900	0.5453	2.051	1.910
2.50	0.0	0.2811	0.1009	0.5627	0.2019	0.4220	1.569	1.481
3.00	0.0	0.2309	0.0739	0.4454	0.1477	0.3340	1.232	1.174
4.00	0.0	0.1600	0.0441	0.2959	0.0882	0.2219	0.8102	0.7820
5.00	0.0	0.1154	0.0291	0.2093	0.0583	0.1570	0.5691	0.5536
6.00	0.0	0.0864	0.0206	0.1552	0.0413	0.1163	0.4198	0.4106
7.00	0.0	0.0667	0.0154	0.1193	0.0307	0.0894	0.3215	0.3157
8.00	0.0	0.0529	0.0119	0.0944	0.0237	0.0708	0.2536	0.2498
9.00	0.0	0.0428	0.0094	0.0764	0.0189	0.0573	0.2049	0.2023
10.00	0.0	0.0354	0.0077	0.0631	0.0154	0.0473	0.1688	0.1670

[a]Orbitals from P. Bagus and T. L. Gilbert, Argonne National Laboratory (unpublished work).

Table VIII

Octupole polarizabilities of Neon at imaginary frequencies (in atomic units) $\alpha_\ell(u)$[a]

u	$1s \rightarrow f$	$2s \rightarrow f$	$2p_{\pm1} \rightarrow d_{\pm1}$	$2p_{\pm1} \rightarrow g_{\pm1}$	$2p_o \rightarrow d_o$	$2p_o \rightarrow g_o$	$\alpha_3^o(u)$	$\alpha_3^o(u) + \alpha_3^1(u)$
0.0	0.0	1.270	7.304	7.512	10.956	6.010	33.052	31.898
0.10	0.0	1.269	7.227	7.480	10.840	5.984	32.800	31.666
0.30	0.0	1.254	6.663	7.239	9.995	5.791	30.942	29.955
0.50	0.0	1.226	5.772	6.810	8.658	5.448	27.914	27.141
0.80	0.0	1.163	4.371	5.982	6.557	4.785	22.858	22.377
1.00	0.0	1.111	3.581	5.402	5.371	4.321	19.786	19.443
1.50	0.0	0.965	2.212	4.104	3.318	3.284	13.883	13.730
2.00	0.0	0.819	1.447	3.125	2.170	2.500	10.062	9.983
2.50	0.0	0.690	1.003	2.420	1.505	1.936	7.554	7.508
3.00	0.0	0.580	0.731	1.912	1.096	1.530	5.848	5.818
4.00	0.0	0.416	0.432	1.263	0.648	1.010	3,770	3.755
5.00	0.0	0.308	0.284	0.887	0.425	0.710	2.614	2.605
6.00	0.0	0.234	0.200	0.654	0.299	0.523	1.911	1.905
7.00	0.0	0.183	0.148	0.500	0.222	0.400	1.454	1.450
8.00	0.0	0.146	0.114	0.394	0.171	0.315	1.141	1.138
9.00	0.0	0.120	0.090	0.318	0.136	0.255	0.918	0.916
10.00	0.0	0.099	0.073	0.262	0.110	0.210	0.754	0.753

[a]Orbitals from P. Bagus and T. L. Gilbert, Argonne National Laboratory (unpublished work).

Table IX

Dipole polarizabilities of Neon at imaginary frequencies (in atomic units) $\alpha_\ell(u)$[1]

u	$1s \rightarrow p$	$2s \rightarrow p$	$2p_{\pm 1} \rightarrow d_{\pm 1}$	$2p_o \rightarrow d_o$	$2p_o \rightarrow s$	$\alpha_1^o(u)$	$\alpha_1^o(u) + \alpha_1^1(u)$
0.0	0.0008	0.0467	1.2885	0.8590	0.7204	2.915	2.255
0.10	0.0008	0.0467	1.2800	0.8532	0.7076	2.888	2.236
0.30	0.0008	0.0461	1.2155	0.8103	0.6207	2.693	2.100
0.50	0.0008	0.0451	1.1095	0.7397	0.5027	2.398	1.893
0.80	0.0008	0.0428	0.9284	0.6189	0.3501	1.941	1.567
1.00	0.0008	0.0409	0.8149	0.5433	0.2763	1.676	1.374
1.50	0.0008	0.0359	0.5882	0.3921	0.1629	1.180	1.002
2.00	0.0008	0.0310	0.4346	0.2900	0.1054	0.8616	0.7522
2.50	0.0008	0.0267	0.3309	0.2206	0.0734	0.6523	0.5819
3.00	0.0008	0.0231	0.2590	0.1726	0.0540	0.5094	0.4622
4.00	0.0008	0.0175	0.1700	0.1132	0.0329	0.3341	0.3105
5.00	0.0008	0.0136	0.1192	0.0795	0.0223	0.2354	0.2223
6.00	0.0008	0.0108	0.0880	0.0587	0.0162	0.1745	0.1667
7.00	0.0008	0.0088	0.0675	0.0500	0.0124	0.1344	0.1295
8.00	0.0008	0.0073	0.0533	0.0355	0.0098	0.1067	0.1034
9.00	0.0008	0.0062	0.0431	0.0287	0.0080	0.0867	0.0845
10.00	0.0008	0.0053	0.0355	0.0237	0.0067	0.0719	0.0703

[1] Hartree-Fock orbitals from, E. Clementi, IBM J. Res. Develop., 9, 2 (1965).

Table X

Quadrupole polarizabilities of Neon at imaginary frequencies (in atomic units) $\alpha_\ell(u)$[1]

u	$1s \rightarrow d$	$2s \rightarrow d$	$2p_{\pm1} \rightarrow p_{\pm1}$	$2p_{\pm1} \rightarrow f_{\pm1}$	$2p_o \rightarrow p_o$	$2p_o \rightarrow f_o$	$\alpha_2^o(u)$	$\alpha_2^o(u) + \alpha_2^1(u)$
0.0	0.0001	0.6027	0.8537	1.8958	1.7074	1.4218	6.482	4.822
0.10	0.0001	0.6015	0.8414	1.8856	1.6829	1.4142	6.426	4.801
0.30	0.0001	0.5919	0.7558	1.8092	1.5117	1.3569	6.026	4.641
0.50	0.0001	0.5737	0.6316	1.6791	1.2632	1.2593	5.407	4.344
0.80	0.0001	0.5344	0.4574	1.4445	0.9148	1.0833	4.434	3.766
1.00	0.0001	0.5031	0.3676	1.2900	0.7352	0.9674	3.863	3.710
1.50	0.0001	0.4207	0.2225	0.9635	0.4451	0.7226	2.774	2.526
2.00	0.0001	0.3448	0.1453	0.7288	0.2905	0.5466	2.056	1.914
2.50	0.0001	0.2816	0.1011	0.5638	0.2021	0.4229	1.571	1.484
3.00	0.0001	0.2311	0.0739	0.4461	0.1479	1.3346	1.234	1.176
4.00	0.0001	0.1601	0.0442	0.2964	0.0883	0.2223	0.8113	0.7831
5.00	0.0001	0.1155	0.0292	0.2096	0.0584	0.1572	0.5698	1.5544
6.00	0.0001	0.0864	0.0207	0.1554	0.0413	0.1165	0.4203	0.4111
7.00	0.0001	0.0667	0.0154	0.1194	0.0307	0.0896	0.3218	0.3161
8.00	0.0001	0.0529	0.0119	0.0845	0.0238	0.0709	0.2539	0.2501
9.00	0.0000	0.0429	0.0094	0.0765	0.0189	0.0574	0.2051	0.2025
10.00	0.0000	0.0354	0.0077	0.0632	0.0154	0.0474	0.1690	0.1671

[1]Hartree-Fock orbitals from, E. Clementi, IBM, J. Res. Develop., 9, 2 (1965).

Table XI

Octupole polarizabilities of Neon at imaginary frequencies (in atomic units) $\alpha_\ell(u)$[1]

u	$1s \rightarrow f$	$2s \rightarrow f$	$2p_{+1} \rightarrow d_{+1}$	$2p_{+1} \rightarrow g_{+1}$	$2p_o \rightarrow d_o$	$2p_o \rightarrow g_o$	$\alpha_3^o(u)$	$\alpha_3^o(u) + \alpha_3^1(u)$
0.0	0.0	1.341	7.854	8.170	11.781	6.536	35.682	34.533
0.10	0.0	1.339	7.761	8.129	11.641	6.503	35.373	34.244
0.30	0.0	1.322	7.092	7.821	10.638	6.257	33.129	32.151
0.50	0.0	1.289	6.067	7.288	9.101	5.831	29.575	28.813
0.80	0.0	1.216	4.522	6.304	6.782	5.043	23.867	23.395
1.00	0.0	1.156	3.677	5.643	5.515	4.515	20.507	20.170
1.50	0.0	0.995	2.249	4.224	3.374	3.379	14.221	14.069
2.00	0.0	0.838	1.465	3.190	2.198	2.552	10.243	10.164
2.50	0.0	0.701	1.014	2.460	1.521	1.968	7.664	7.617
3.00	0.0	0.588	0.738	1.939	1.107	1.551	5.922	5.891
4.00	0.0	0.420	0.436	1.277	0.654	1.022	3.810	3.794
5.00	0.0	0.310	0.286	0.897	0.429	0.717	2.639	2.630
6.00	0.0	0.236	0.201	0.660	0.302	0.528	1.928	1.922
7.00	0.0	0.184	0.149	0.505	0.224	0.404	1.466	1.462
8.00	0.0	0.147	0.115	0.340	0.172	0.318	1.150	1.148
9.00	0.0	0.120	0.091	0.321	0.137	0.257	0.926	0.924
10.00	0.0	0.100	0.074	0.264	0.111	0.211	0.760	0.759

[1] Hartree-Fock orbitals from, E. Clementi, IBM, J. Res. Develop., 9, 2 (1965).

Table XII

Dipole polarizabilities of Na^+ at imaginary frequencies (in atomic units) $\alpha_\ell(u)$[1]

u	$1s \rightarrow p$	$2s \rightarrow p$	$2p_{\pm 1} \rightarrow d_{\pm 1}$	$2p_o \rightarrow d_o$	$2p_o \rightarrow s$	$\alpha_1^o(u)$	$\alpha_1^o(u) + \alpha_1^1(u)$
0.0	0.0007	0.0342	0.5340	0.3560	0.2050	1.130	0.9160
0.1	0.0007	0.0342	0.5327	0.3551	0.2039	1.127	0.9137
0.3	0.0007	0.0339	0.5229	0.3486	0.1956	1.102	0.8954
0.5	0.0007	0.0335	0.5047	0.3364	0.1810	1.056	0.8620
0.8	0.0007	0.0325	0.4661	0.3107	0.1538	0.9638	0.7938
1.00	0.0006	0.0317	0.4364	0.2909	0.1355	0.8951	0.7426
1.50	0.0006	0.0292	0.3606	0.2404	0.0969	0.7278	0.6162
2.00	0.0006	0.0264	0.2940	0.1960	0.0701	0.5871	0.5071
2.50	0.0006	0.0237	0.2402	0.1601	0.0520	0.4766	0.4190
3.00	0.0006	0.0211	0.1979	0.1320	0.0398	0.3914	0.3494
4.00	0.0006	0.0168	0.1390	0.0927	0.0252	0.2742	0.2507
5.00	0.0005	0.0136	0.1019	0.0679	0.0173	0.2012	0.1871
6.00	0.0005	0.0111	0.0775	0.0517	0.0126	0.1533	0.1444
7.00	0.0005	0.0092	0.0607	0.0405	0.0096	0.1205	0.1146
8.00	0.0005	0.0077	0.0487	0.0325	0.0076	0.0971	0.0930
9.00	0.0005	0.0066	0.0399	0.0266	0.0062	0.0798	0.0769
10.00	0.0005	0.0057	0.0333	0.0222	0.0051	0.0667	0.0646

[1] Hartree-Fock orbitals from, E. Clementi, IBM, J. Res. Develop., 9, 2 (1965).

Table XIII

Quadrupole polarizabilities of Na^+ at imaginary frequencies (in atomic units) $\alpha_\ell(u)$[1]

u	$1s \rightarrow d$	$2s \rightarrow d$	$2p_{\pm1} \rightarrow p_{\pm1}$	$2p_{\pm1} \rightarrow f_{\pm1}$	$2p_o \rightarrow p_o$	$2p_o \rightarrow f_o$	$\alpha_2^o(u)$	$\alpha_2^o(u) + \alpha_2^1(u)$
0.0	0.0	0.2245	0.1805	0.4405	0.3610	0.3303	0.5369	1.2640
0.10	0.0	0.2243	0.1797	0.4397	0.3595	0.3298	1.5331	1.2620
0.30	0.0	0.2227	0.1737	0.4341	0.3475	0.3256	1.5036	1.2457
0.50	0.0	0.2195	0.1630	0.4234	0.3249	0.3175	1.4493	1.2144
0.80	0.0	0.2121	0.1419	0.3999	0.2838	0.2999	1.3377	1.1452
1.00	0.0	0.2058	0.1271	0.3809	0.2542	0.2857	1.2537	1.0891
1.50	0.0	0.1867	0.0940	0.3294	0.1880	0.2471	1.0451	0.9366
2.00	0.0	0.1655	0.0695	0.2798	0.1390	0.2099	0.8638	0.7913
2.50	0.0	0.1448	0.0524	0.2366	0.1049	0.1774	0.7161	0.6661
3.00	0.0	0.1259	0.0405	0.2005	0.0810	0.1504	0.5983	0.5626
4.00	0.0	0.0950	0.0258	0.1467	0.0516	0.1100	0.4291	0.4094
5.00	0.0	0.0726	0.0177	0.1105	0.0354	0.0829	0.3190	0.3072
6.00	0.0	0.0565	0.0128	0.0856	0.0256	0.0642	0.2447	0.2373
7.00	0.0	0.0449	0.0097	0.0679	0.0194	0.0510	0.1928	0.1879
8.00	0.0	0.0363	0.0076	0.0551	0.0151	0.0413	0.1554	0.1520
9.00	0.0	0.0299	0.0061	0.0455	0.0121	0.0341	0.1276	0.1252
10.00	0.0	0.0250	0.0050	0.0381	0.0099	0.0286	0.1065	0.1048

[1]Hartree-Fock orbitals from, E. Clementi, IBM, J. Res. Develop., 9, 2 (1965).

Table XIV

Octupole polarizabilities of Na^+ at imaginary frequencies (in atomic units) $\alpha_\ell(u)$[1]

u	$1s \rightarrow f$	$2s \rightarrow f$	$2p_{\pm1} \rightarrow d_{\pm1}$	$2p_{\pm1} \rightarrow g_{\pm1}$	$2p_o \rightarrow d_o$	$2p_o \rightarrow g_o$	$\alpha_3^o(u)$	$\alpha_3^o(u) + \alpha_3^1(u)$
0.0	0.0	0.3209	1.0059	1.0254	1.5089	0.8203	4.6814	4.5411
0.10	0.0	0.3207	1.0023	0.0240	1.5034	0.8192	4.6695	4.5301
0.30	0.0	0.3190	0.9741	1.0125	1.4612	0.8100	4.5768	4.4443
0.50	0.0	0.3158	0.9226	0.9904	1.3839	0.7923	4.4050	4.2849
0.80	0.0	0.3082	0.8181	0.9415	1.2271	0.7532	4.0481	3.9513
1.00	0.0	0.3014	0.7413	0.9015	1.1120	0.7212	3.7775	3.6965
1.50	0.0	0.2806	0.5611	0.7899	0.8417	0.6319	3.1052	3.0562
2.00	0.0	0.2562	0.4202	0.6790	0.6303	0.5432	2.5290	2.4996
2.50	0.0	0.2308	0.3184	0.5797	0.4776	0.4638	2.0704	2.0520
3.00	0.0	0.2063	0.2460	0.4950	0.3690	0.3960	1.7124	1.7001
4.00	0.0	0.1633	0.1561	0.3657	0.2342	0.2926	1.2119	1.2055
5.00	0.0	0.1295	0.1063	0.2770	0.1595	0.2216	0.8939	0.8899
6.00	0.0	0.1037	0.0766	0.2152	0.1149	0.1721	0.6824	0.6798
7.00	0.0	0.0817	0.0576	0.1710	0.0863	0.1368	0.5359	0.5340
8.00	0.0	0.0693	0.0447	0.1387	0.0671	0.1109	0.4307	0.4294
9.00	0.0	0.0578	0.0357	0.1144	0.0536	0.0915	0.3531	0.3521
10.00	0.0	0.0488	0.0292	0.0959	0.0438	0.0767	0.2942	0.2934

[1]Hartree-Fock orbitals from, E. Clementi, IBM, J. Res. Develop., 9, 2 (1965).

Table XV

Dipole polarizabilities of Mg^{2+} at imaginary frequencies (in atomic units) $\alpha_\ell(u)$[1]

u	$1s \rightarrow p$	$2s \rightarrow p$	$2p_{\pm1} \rightarrow d_{\pm1}$	$2p_0 \rightarrow d_0$	$2p_0 \rightarrow s$	$\alpha_1^0(u)$	$\alpha_1^0(u) + \alpha_1^1(u)$
0.0	0.0004	0.0241	0.2686	0.1791	0.0784	0.5506	0.4596
0.10	0.0004	0.0241	0.2683	0.1789	0.0782	0.5500	0.4591
0.30	0.0004	0.0240	0.2660	0.1774	0.0769	0.5447	0.4551
0.50	0.0004	0.0239	0.2616	0.1744	0.0743	0.5346	0.4475
0.80	0.0004	0.0235	0.2515	0.1676	0.0689	0.5119	0.4302
1.00	0.0004	0.0231	0.2429	0.1619	0.0646	0.4929	0.4158
1.50	0.0004	0.0219	0.2179	0.1453	0.0532	0.4387	0.3742
2.00	0.0004	0.0205	0.1914	0.1276	0.0430	0.3828	0.3307
2.50	0.0004	0.0190	0.1664	0.1109	0.0346	0.3313	0.2898
3.00	0.0004	0.0175	0.1442	0.0962	0.0281	0.2863	0.2535
4.00	0.0004	0.0146	0.1091	0.0727	0.0191	0.2159	0.1951
5.00	0.0004	0.0123	0.0840	0.0560	0.0136	0.1663	0.1527
6.00	0.0004	0.0103	0.0661	0.0441	0.0102	0.1310	0.1219
7.00	0.0004	0.0088	0.0531	0.0354	0.0078	0.1055	0.0992
8.00	0.0003	0.0075	0.0435	0.0290	0.0062	0.0865	0.0820
9.00	0.0003	0.0065	0.0362	0.0241	0.0051	0.0722	0.0688
10.00	0.0003	0.0056	0.0305	0.0203	0.0042	0.0610	0.0585

[1]Hartree-Fock orbitals from, E. Clementi, IBM, J. Res. Develop., 9, 2 (1965).

Table XVI

Quadrupole polarizabilities of Mg^{2+} at imaginary frequencies (in atomic units) $\alpha_\ell(u)$[1]

u	$1s \rightarrow d$	$2s \rightarrow d$	$2p_{\pm1} \rightarrow p_{\pm1}$	$2p_{\pm1} \rightarrow f_{\pm1}$	$2p_o \rightarrow p_o$	$2p_o \rightarrow f_o$	$\alpha_2^o(u)$	$\alpha_2^o(u) + \alpha_2^1(u)$
0.0	0.0	0.0998	0.0560	0.1453	0.1120	0.1090	0.5221	0.4515
0.10	0.0	0.0997	0.0559	0.1452	0.1118	0.1089	0.5216	0.4512
0.30	0.0	0.0993	0.0551	0.1444	0.1103	0.1083	0.5174	0.4484
0.50	0.0	0.0985	0.0536	0.1429	0.1072	0.1072	0.5094	0.4431
0.80	0.0	0.0967	0.0503	0.1392	0.1005	0.1044	0.491,	0.4306
1.00	0.0	0.0950	0.0476	0.1361	0.0951	0.1021	0.4758	0.4199
1.50	0.0	0.0896	0.0401	0.1264	0.0803	0.0948	0.4313	0.3871
2.00	0.0	0.0831	0.0331	0.1153	0.0662	0.0865	0.3842	0.3502
2.50	0.0	0.0761	0.0271	0.1041	0.0542	0.0780	0.3395	0.3134
3.00	0.0	0.0691	0.0223	0.0933	0.0445	0.0700	0.2992	0.2790
4.00	0.0	0.0561	0.0154	0.0746	0.0308	0.0560	0.2330	0.2205
5.00	0.0	0.0454	0.1111	0.0600	0.0222	0.0450	0.1837	0.1756
6.00	0.0	0.0370	0.0083	0.0487	0.0166	0.0366	0.1471	0.1416
7.00	0.0	0.0303	0.0064	0.0401	0.0128	0.0301	0.1197	0.1160
8.00	0.0	0.0251	0.0051	0.0335	0.0102	0.0251	0.0990	0.0962
9.00	0.0	0.0211	0.0041	0.0283	0.0082	0.0212	0.0829	0.0809
10.00	0.0	0.0179	0.0034	0.0241	0.0068	0.0181	0.0703	0.0688

[1]Hartree-Fock orbitals from, E. Clementi, IBM, J. Res. Develop., 9, 2 (1965).

Table XVII

Octupole polarizabilities of Mg^{2+} at imaginary frequencies (in atomic units) $\alpha_\ell(u)$[1]

u	$1s \rightarrow f$	$2s \rightarrow f$	$2p_{\pm1} \rightarrow d_{\pm1}$	$2p_{\pm1} \rightarrow g_{\pm1}$	$2p_o \rightarrow d_o$	$2p_o \rightarrow g_o$	$\alpha_3^o(u)$	$\alpha_3^o(u) + \alpha_3^1(u)$
0.0	0.0	0.1045	0.2157	0.2167	0.3235	0.1734	1.0339	1.0067
0.10	0.0	0.1045	0.2154	0.2166	0.3231	0.1733	1.0328	1.0057
0.30	0.0	0.1042	0.2128	0.2156	0.3192	0.1725	1.0242	0.9978
0.50	0.0	0.1036	0.2078	0.2137	0.3116	0.1710	1.0076	0.9824
0.80	0.0	0.1022	0.1965	0.2091	0.2948	0.1623	0.9700	0.9473
1.00	0.0	0.1010	0.1872	0.2051	0.2808	0.1461	0.9383	0.9176
1.50	0.0	0.0970	0.1609	0.1926	0.2413	0.1541	0.8459	0.8305
2.00	0.0	0.0919	0.1346	0.1780	0.2019	0.1424	0.7487	0.7377
2.50	0.0	0.0862	0.1114	0.1625	0.1670	0.1300	0.6572	0.6495
3.00	0.0	0.0801	0.0921	0.1475	0.1381	0.1180	0.5757	0.5703
4.00	0.0	0.0682	0.0640	0.1203	0.0960	0.0962	0.4447	0.4417
5.00	0.0	0.0575	0.0400	0.0981	0.0691	0.0785	0.3492	0.3474
6.00	0.0	0.0483	0.0343	0.0806	0.0515	0.0645	0.2792	0.2780
7.00	0.0	0.0408	0.0264	0.0669	0.0396	0.0535	0.2272	0.2263
8.00	0.0	0.0346	0.0208	0.0561	0.0313	0.0449	0.1877	0.1871
9.00	0.0	0.0296	0.0168	0.0476	0.0252	0.0381	0.1573	0.1568
10.00	0.0	0.0255	0.0139	0.0408	0.0208	0.0326	0.1335	0.1331

[1]Hartree-Fock orbitals from, E. Clementi, IBM, J. Res. Develop., 9, 2 (1965).

Table XVIII

Dipole polarizabilities of Al^{3+} at imaginary frequencies (in atomic units) $\alpha_\ell(u)$[1]

u	$1s \rightarrow p$	$2s \rightarrow p$	$2p_{\pm 1} \rightarrow d_{\pm 1}$	$2p_o \rightarrow d_o$	$2p_o \rightarrow s$	$\alpha_1^o(u)$	$\alpha_1^o(u) + \alpha_1^1(u)$
0.0	0.0003	0.0171	0.1517	0.1011	0.0358	0.3060	0.2607
0.10	0.0003	0.0171	0.1516	0.1011	0.0358	0.3059	0.2606
0.30	0.0003	0.0171	0.1509	0.1006	0.0355	0.3044	0.2594
0.50	0.0003	0.0170	0.1496	0.0997	0.0349	0.3014	0.2571
0.80	0.0003	0.0168	0.1463	0.0976	0.0336	0.2945	0.2518
1.00	0.0003	0.0166	0.1435	0.0957	0.0324	0.2885	0.2471
1.50	0.0003	0.0161	0.1346	0.0897	0.0290	0.2697	0.2325
2.00	0.0003	0.0154	0.1241	0.0827	0.0254	0.2478	0.2152
2.50	0.0003	0.0146	0.1130	0.0753	0.0219	0.2251	0.1971
3.00	0.0003	0.0138	0.1021	0.0681	0.0188	0.2031	0.1794
4.00	0.0003	0.0120	0.0827	0.0551	0.0139	0.1641	0.1473
5.00	0.0003	0.0105	0.0670	0.0447	0.0105	0.1329	0.1211
6.00	0.0003	0.0091	0.0548	0.0365	0.0081	0.1087	0.1002
7.00	0.0002	0.0079	0.0453	0.0302	0.0064	0.0900	0.0838
8.00	0.0002	0.0060	0.0379	0.0253	0.0052	0.0754	0.0708
9.00	0.0002	0.0061	0.0321	0.0214	0.0042	0.0640	0.0605
10.00	0.0002	0.0053	0.0274	0.0183	0.0035	0.0548	0.0522

[1] Hartree-Fock orbitals from, E. Clementi, IBM, J. Res. Develop., 9, 2 (1965).

Table XIX

Quadrupole polarizabilities of Al^{3+} at imaginary frequencies (in atomic units) $\alpha_\ell(u)$[1]

u	$1s \rightarrow d$	$2s \rightarrow d$	$2p_{\pm1} \rightarrow p_{\pm1}$	$2p_{\pm1} \rightarrow f_{\pm1}$	$2p_o \rightarrow p_o$	$2p_o \rightarrow f_o$	$\alpha_2^o(u)$	$\alpha_2^o(u) + \alpha_2^1(u)$
0.0	0.0	0.0491	0.0217	0.0586	0.0433	0.0440	0.2166	0.1930
0.10	0.0	0.0491	0.0216	0.0586	0.0433	0.0440	0.2165	0.1929
0.30	0.0	0.0489	0.0215	0.0585	0.0429	0.0438	0.2157	0.1923
0.50	0.0	0.0487	0.0212	0.0581	0.0423	0.0436	0.2139	0.1910
0.80	0.0	0.0481	0.0205	0.0574	0.0409	0.0430	0.2099	0.1881
1.00	0.0	0.0476	0.0199	0.0567	0.0397	0.0425	0.2064	0.1854
1.50	0.0	0.0459	0.0180	0.0544	0.0361	0.0408	0.1953	0.1770
2.00	0.0	0.0438	0.0160	0.0516	0.0320	0.0387	0.1822	0.1666
2.50	0.0	0.0413	0.0140	0.0485	0.0280	0.0364	0.1682	0.1551
3.00	0.0	0.0386	0.0122	0.0452	0.0243	0.0339	0.1543	0.1435
4.00	0.0	0.0333	0.0092	0.0388	0.0183	0.0291	0.1287	0.1212
5.00	0.0	0.0283	0.0070	0.0331	0.0140	0.0248	0.1071	0.1018
6.00	0.0	0.0239	0.0055	0.0281	0.0109	0.0211	0.0895	0.0857
7.00	0.0	0.0203	0.0043	0.0240	0.0087	0.0180	0.0754	0.0726
8.00	0.0	0.0173	0.0035	0.0207	0.0070	0.0155	0.0640	0.0619
9.00	0.0	0.0148	0.0029	0.0179	0.0058	0.0134	0.0548	0.0532
10.00	0.0	0.0128	0.0024	0.0156	0.0048	0.0117	0.0473	0.0461

[1]Hartree-Fock orbitals from, E. Clementi, IBM, J. Res. Develop., 9, 2 (1965).

Table XX

Octupole polarizabilities of Al^{3+} at imaginary frequencies (in atomic units) $\alpha_\ell(u)$[1]

u	$1s \rightarrow f$	$2s \rightarrow f$	$2p_{\pm1} \rightarrow d_{\pm1}$	$2p_{\pm1} \rightarrow g_{\pm1}$	$2p_o \rightarrow d_o$	$2p_o \rightarrow g_o$	$\alpha_3^o(u)$	$\alpha_3^o(u) + \alpha_3^1(u)$
0.0	0.0	0.0395	0.0619	0.0616	0.0929	0.0493	0.3050	0.2980
0.10	0.0	0.0395	0.0619	0.0616	0.0928	0.0492	0.3049	0.2979
0.30	0.0	0.0394	0.0615	0.0614	0.0922	0.0491	0.3036	0.2967
0.50	0.0	0.0393	0.0607	0.0611	0.0911	0.0489	0.3011	0.2944
0.80	0.0	0.0390	0.0590	0.0605	0.0885	0.0484	0.2953	0.2889
1.00	0.0	0.0387	0.0575	0.0599	0.0862	0.0479	0.2901	0.2841
1.50	0.0	0.0377	0.0527	0.0580	0.0791	0.0464	0.2739	0.2688
2.00	0.0	0.0365	0.0473	0.0555	0.0710	0.0444	0.2547	0.2506
2.50	0.0	0.0351	0.0418	0.0527	0.0627	0.0421	0.2344	0.2312
3.00	0.0	0.0334	0.0366	0.0497	0.0549	0.0397	0.2144	0.2119
4.00	0.0	0.0300	0.0279	0.0435	0.0418	0.0348	0.1779	0.1765
5.00	0.0	0.0265	0.0213	0.0377	0.0320	0.0302	0.1478	0.1468
6.00	0.0	0.0232	0.0166	0.0326	0.0249	0.0261	0.1235	0.1228
7.00	0.0	0.0203	0.0132	0.0283	0.0197	0.0226	0.1041	0.1036
8.00	0.0	0.0178	0.0106	0.0245	0.0159	0.0196	0.0885	0.0882
9.00	0.0	0.0156	0.0087	0.0214	0.0131	0.0171	0.0759	0.0757
10.00	0.0	0.0137	0.0073	0.0188	0.0109	0.0150	0.0657	0.0655

[1]Hartree-Fock orbitals from, E. Clementi, IBM, J. Res. Develop., 9, 2 (1965).

Table XXI

Dipole polarizabilities of Si^{4+} at imaginary frequencies (in atomic units) $\alpha_\ell(u)$[1]

u	$1s \rightarrow p$	$2s \rightarrow$	$2p_{\pm 1} \rightarrow d_{\pm 1}$	$2p_o \rightarrow d_o$	$2p_o \rightarrow s$	$\alpha_1^o(u)$	$\alpha_1^o(u) + \alpha_1^1(u)$
0.0	0.0002	0.0123	0.0928	0.0618	0.0185	0.1856	0.1605
0.10	0.0002	0.0123	0.0927	0.0618	0.0185	0.1855	0.1605
0.30	0.0002	0.0123	0.0924	0.0616	0.0184	0.1850	0.1601
0.50	0.0002	0.0123	0.0919	0.0613	0.0182	0.1839	0.1593
0.80	0.0002	0.0122	0.0908	0.0605	0.0178	0.1815	0.1573
1.00	0.0002	0.0121	0.0897	0.0598	0.0175	0.1793	0.1556
1.50	0.0002	0.0118	0.0862	0.0575	0.0164	0.1721	0.1499
2.00	0.0002	0.0115	0.0818	0.0546	0.0151	0.1631	0.1428
2.50	0.0002	0.0111	0.0769	0.0513	0.0137	0.1531	0.1347
3.00	0.0002	0.0106	0.0717	0.0478	0.0123	0.1426	0.1262
4.00	0.0002	0.0096	0.0614	0.0409	0.0098	0.1220	0.1093
5.00	0.0002	0.0086	0.0521	0.0348	0.0078	0.1035	0.0938
6.00	0.0002	0.0077	0.0442	0.0295	0.0063	0.0879	0.0805
7.00	0.0002	0.0068	0.0377	0.0251	0.0051	0.0749	0.0693
8.00	0.0002	0.0061	0.0323	0.0215	0.0042	0.0643	0.0599
9.00	0.0002	0.0054	0.0278	0.0186	0.0035	0.0556	0.0521
10.00	0.0002	0.0049	0.0242	0.0161	0.0030	0.0484	0.0457

[1] Hartree-Fock orbitals from, E. Clementi, IBM, J. Res. Develop., 9, 2 (1965).

Table XXII

Quadrupole polarizabilities of Si^{4+} at imaginary frequencies (in atomic units) $\alpha_\ell(u)$[1]

u	$1s \rightarrow d$	$2s \rightarrow d$	$2p_{\pm1} \rightarrow p_{\pm1}$	$2p_{\pm1} \rightarrow f_{\pm1}$	$2p_o \rightarrow p_o$	$2p_o \rightarrow f_o$	$\alpha_2^o(u)$	$\alpha_2^o(u) + \alpha_2^1(u)$
0.0	0.0	0.0261	0.0097	0.0270	0.0193	0.0203	0.1024	0.0930
0.10	0.0	0.0261	0.0097	0.0270	0.0193	0.0203	0.1024	0.0930
0.30	0.0	0.0261	0.0096	0.0270	0.0192	0.0202	0.1022	0.0928
0.50	0.0	0.0260	0.0096	0.0269	0.0191	0.0202	0.1017	0.0925
0.80	0.0	0.0258	0.0094	0.0267	0.0187	0.0200	0.1006	0.0916
1.00	0.0	0.0256	0.0092	0.0265	0.0184	0.0199	0.0996	0.0909
1.50	0.0	0.0250	0.0087	0.0259	0.0174	0.0194	0.0964	0.0883
2.00	0.0	0.0242	0.0081	0.0251	0.0161	0.0188	0.0923	0.0850
2.50	0.0	0.0233	0.0074	0.0241	0.0148	0.0181	0.0877	0.0812
3.00	0.0	0.0222	0.0067	0.0231	0.0134	0.0173	0.0827	0.0770
4.00	0.0	0.0200	0.0054	0.0208	0.0109	0.0156	0.0727	0.0683
5.00	0.0	0.0177	0.0044	0.0185	0.0088	0.0139	0.0633	0.0600
6.00	0.0	0.0155	0.0036	0.0164	0.0071	0.0123	0.0550	0.0525
7.00	0.0	0.0136	0.0030	0.0145	0.0059	0.0109	0.0478	0.0458
8.00	0.0	0.0119	0.0024	0.0129	0.0049	0.0096	0.0417	0.0402
9.00	0.0	0.0104	0.0020	0.0114	0.0041	0.0086	0.0365	0.0353
10.00	0.0	0.0092	0.0017	0.0101	0.0035	0.0076	0.0321	0.0312

[1]Hartree-Fock orbitals from, E. Clementi, IBM, J. Res. Develop. 9, 2 (1965).

Table XXIII

Octupole polarizabilities of Si^{4+} at imaginary frequencies (in atomic units) $\alpha_\ell(u)$[1]

u	$1s \rightarrow f$	$2s \rightarrow f$	$2p_{\pm1} \rightarrow d_{\pm1}$	$2p_{\pm1} \rightarrow g_{\pm1}$	$2p_o \rightarrow d_o$	$2p_o \rightarrow g_o$	$\alpha_3^o(u)$	$\alpha_3^o(u) + \alpha_3^1(u)$
0.0	0.0	0.0167	0.0215	0.0212	0.0322	0.0170	0.0086	0.1064
0.10	0.0	0.0167	0.0215	0.0212	0.0322	0.0170	0.1085	0.1063
0.30	0.0	0.0167	0.0214	0.0212	0.0321	0.0170	0.1083	0.1061
0.50	0.0	0.0166	0.0213	0.0211	0.0319	0.0169	0.1078	0.1056
0.80	0.0	0.0165	0.0209	0.0210	0.0314	0.0168	0.1066	0.1045
1.00	0.0	0.0165	0.0206	0.0209	0.0309	0.0167	0.1055	0.1035
1.50	0.0	0.0162	0.0196	0.0205	0.0293	0.0164	0.1020	0.1002
2.00	0.0	0.0159	0.0183	0.0200	0.0274	0.0160	0.0975	0.0960
2.50	0.0	0.0154	0.0169	0.0194	0.0253	0.0155	0.0925	0.0911
3.00	0.0	0.0150	0.0154	0.0187	0.0231	0.0149	0.0871	0.0860
4.00	0.0	0.0139	0.0126	0.0172	0.0190	0.0137	0.0763	0.0756
5.00	0.0	0.0127	0.0103	0.0156	0.0154	0.0125	0.0664	0.0659
6.00	0.0	0.0115	0.0084	0.0140	0.0126	0.0112	0.0577	0.0573
7.00	0.0	0.0104	0.0069	0.0126	0.0103	0.0101	0.0502	0.0500
8.00	0.0	0.0094	0.0057	0.0113	0.0085	0.0090	0.0439	0.0437
9.00	0.0	0.0084	0.0048	0.0101	0.0072	0.0081	0.0385	0.0384
10.00	0.0	0.0076	0.0040	0.0091	0.0061	0.0073	0.0340	0.0339

[1]Hartree-Fock orbitals from, E. Clementi, IBM, J. Res. Develop., 9, 2 (1965).

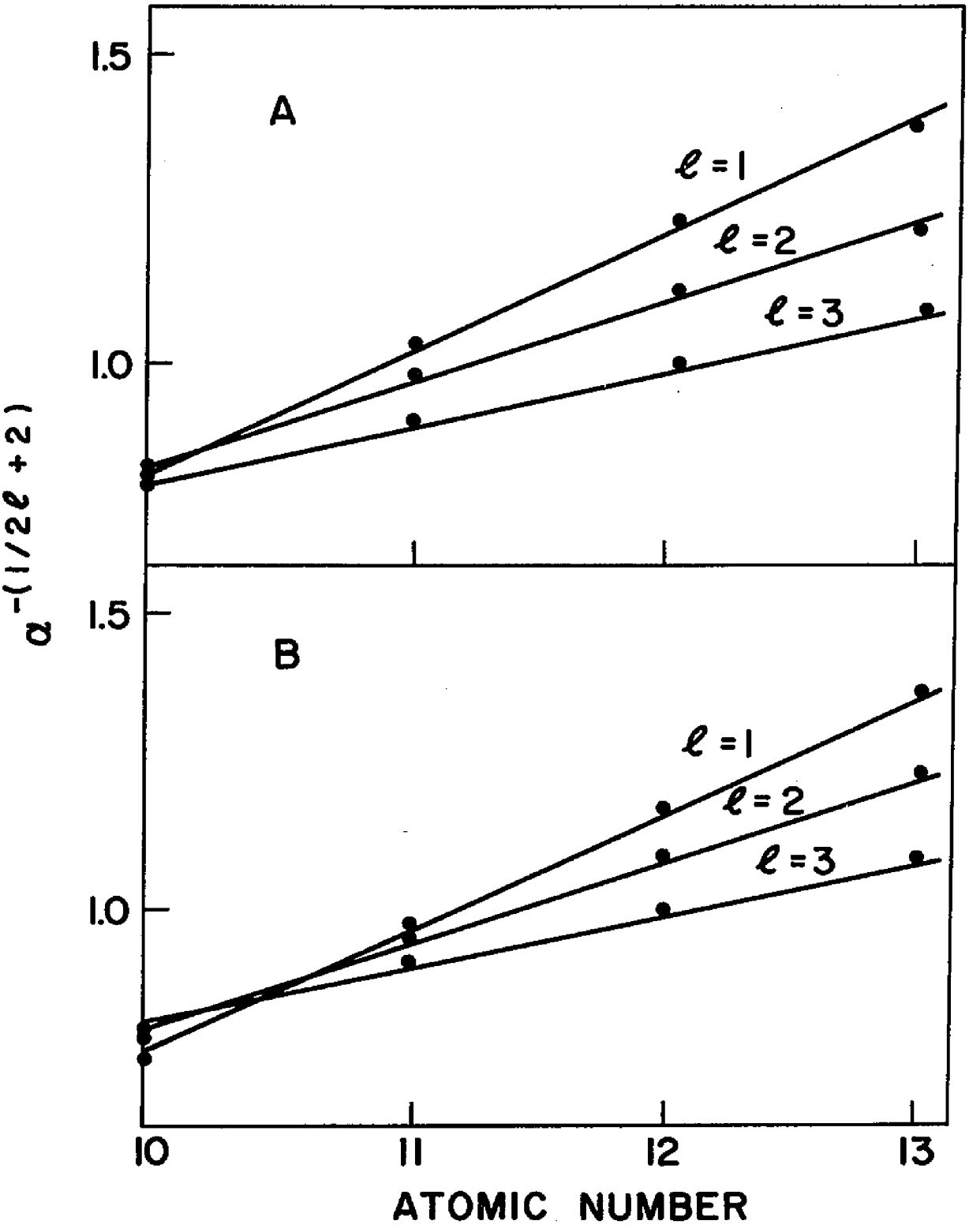
Figure 1. Multipole polarizabilities as a function of atomic number for the Neon isoelectronic series. Best least squares fit.

(A) With Correlation

1. $\alpha_1^{-1/4}$ versus Z
2. $\alpha_2^{-1/6}$ versus Z
3. $\alpha_3^{-1/8}$ versus Z

(B) Without Correlation

1. $\alpha_1^{-1/4}$ versus Z
2. $\alpha_2^{-1/6}$ versus Z
3. $\alpha_3^{-1/8}$ versus Z


1.5
1.0
A
ℓ = 1
ℓ = 2
ℓ = 3
$\alpha^{-(1/2\ell+2)}$
1.5
1.0
B
ℓ = 1
ℓ = 2
ℓ = 3
10
11
12
13
ATOMIC NUMBER

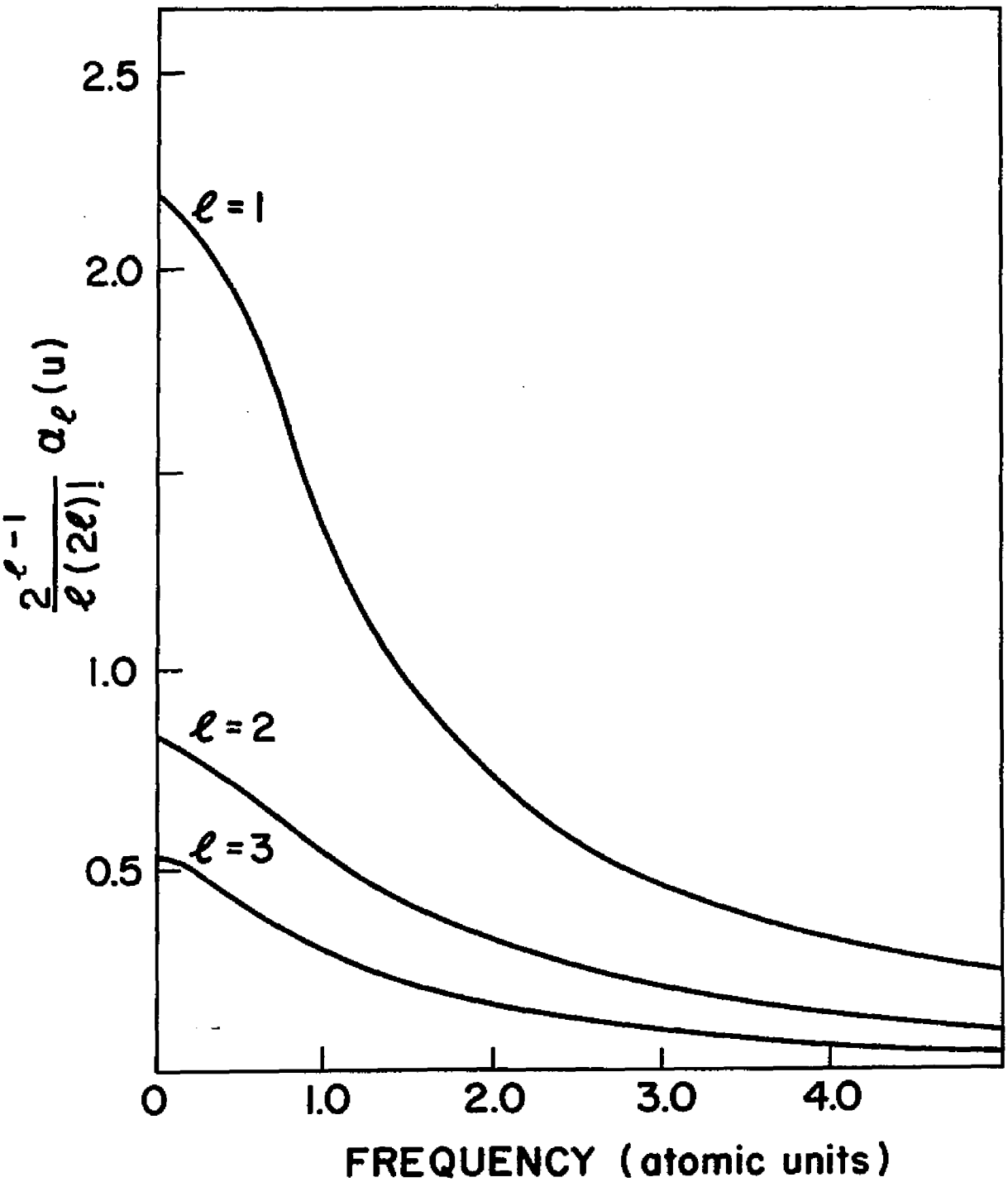
power of the atomic number. Dipole polarizabilities are shown to be proportional to Z^{-4}, quadrupole polarizabilities to Z^{-6}, and octupole polarizabilities proportional to Z^{-8}.[19] From the least-squares fit of the data in Figure 1, an approximate formula for dipole polarizabilities as a function of nuclear charge is:

$$\alpha_1(0) \cong 759.31(Z-5.669)^{-4} \text{ (in atomic units)}$$

Similar formulas for quadrupole and octupole polarizabilities can also be obtained. Formulas of this type may be used to extrapolate $\alpha_\ell(0)$ for other ten electron ions with larger charges.

Polarizabilities decrease smoothly as a function of imaginary frequency; this smooth decrease can be seen in Figure 2 and from the appropriate Tables (VI-XXIII). Real frequency polarizabilities increase (not decrease) smoothly only until a transition frequency at $[\Delta E^2-(h\nu)^2]$ is reached [see equations (48) and (49)]. The experimental polarizabilities do not have singularities because of line width contributions at the poles. These poles correspond to the various excitation energies of the atom. The line width contributions have been neglected because we have used a semi-classical theory. We must use semi-classical theory, however, to obtain the proper form of the polarizability, which when evaluated at imaginary frequencies is useful in equation (30). In a very naive fashion the polarizability at imaginary frequencies corresponds to the linear response to a field which decreases exponentially in time. However, since the time scale is so short, this analogy is limited and its values are probably

Figure 2. Neon multipole polarizabilities as a function of imaginary frequencies. The scales are chosen so that they all behave asymptotically as $1/u^2$.


2.5
2.0
1.0
0.5
$\frac{2^{\ell-1}}{\ell(2\ell)!}\alpha_\ell(u)$
$\ell=1$
$\ell=2$
$\ell=3$
0
1.0
2.0
3.0
4.0
FREQUENCY (atomic units)

meaningless because we used a semi-classical result and furthermore, these polarizabilities can not be experimentally determined due to the time scale involved. In Tables VI-XXIII, only static polarizabilities are directly related to experimentally determined quantities. One could expand the results in the form of equation (58b) and then transform to real frequencies via equation (58a). These numbers would then correspond to the observed frequency-dependent polarizabilities providing line width effects are neglected.

For neutral atoms at imaginary frequencies dipole polarizabilities are smaller than quadrupole polarizabilities which are smaller than octupole polarizabilities. This trend is not observed in the case of more highly charged species. This effect can be seen from the slopes in Figure 1, where each multipole polarizability is proportional to a different inverse power of Z.

When an atom is acted upon by an external field, we would expect to find that the outermost electrons are perturbed more than the inner electrons. This is found to be the case with p_z electrons having the largest contribution to the polarizability. They are larger than the combined p_x and p_y contributions because we have considered the external field to be aligned along the z-axis. The s electrons are found to contribute only a few percent to the total polarizability. This trend seems to occur regardless of the nuclear charge, except that the difference in the $p_{x,y}$ and p_z contributions gradually decreases as the nuclear charge increases.

A comparison of the different multipole polarizabilities can be found in Table II. These comparisons are for static polarizabilities

only. The fully coupled results for large systems are difficult to obtain, and thus only a few values are available. Uncoupled calculations are easier and results for large systems are available. A good compilation of static polarizabilities can be found in the paper by Langhoff and Hurst.[33] Also the papers by Tuan and Wu[34] and Epstein and Johnson[35] present polarizabilities corrected to first-order in electron correlation, but they result from a different uncoupled procedure than ours. In Table II, we find the geometric approximation applied to the uncoupled results of this paper and that of Tuan's. As was previously noted for the two electron results, the ten electron results compare well with the coupled results, especially in the case of dipole polarizabilities. In the case of quadrupole polarizabilities, the correspondence is less noticeable; in fact, the correlation corrections seem to be much too large because values without correlation agree quite closely with the coupled results [see Tables II and IV]. No coupled results are available for octupole polarizabilities, but the available uncoupled results agree with ours.

There are several forms of the uncoupled Hartree-Fock method available for atomic systems. These differ from each other mainly in having different forms for the zero-order Hamiltonians. These methods have been reviewed recently by Langhoff, Karplus and Hurst.[27] The uncoupled procedure used in our calculations is referred to as method d in the article by the above authors. This method used the commutation relation of equation (109), which for ten electron systems is not rigorously correct and introduces slight errors in the calculations. In our calculations, we have also omitted the self-interaction terms

in the Hartree-Fock potential. Omitting this interaction does not alter the zero-order equation, and previous work indicates that these terms, which are an artifact of the Hartree-Fock procedure, cause the results to be less accurate. Tuan and Wu have used an uncoupled method (Method c in Langhoff, Karplus and Hurst) in which commutation is not assumed and also the self-interaction terms in the Hartree-Fock potential are included. Then zero-order results are lower while ours are higher than the coupled results. Correlation corrections increase their zero-order values while it decreases ours, thus both methods do tend to approach the coupled value. These differences are presumed to be due to the self-interaction terms in the Hartree-Fock potential. These different methods have recently been incorporated in a more general theory by Riemenschneider and Kestner, in which the various approximations to the Hartree-Fock Hamiltonian and potential can be systematically studied.[36]

2. Dispersion Coefficients

Dispersion coefficients are presented in Tables III and V. These various interaction coefficients are calculated by means of equation (30). To evaluate equation (30), polarizabilities were calculated to frequencies large enough to use the sum rule procedure of Mavroyannis and Stephens[2] in order to extend the numerical integrations to infinite frequency. For ten electron systems, there are only a few values of long-range forces in the literature, essentially none for C_8 and C_{10} interactions.

In summary; for neon interactions at large distances, we find

$$E_2(R) = -\frac{5.097}{R^6} - \frac{59.72}{R^8} - \frac{327.85 + 697.38}{R^{10}}$$

when electron correlation is included, and

$$E_2(R) = -\frac{7.759}{R^6} - \frac{88.47}{R^8} - \frac{471.45 + 881.27}{R^{10}}$$

before these corrections are added. All of these numbers are in atomic units.

In the past, many discrepancies between experimental and theoretical values of $E_2(R)$ have arisen. This is especially true of the alkali-alkali pairs in which cases the theoretical values are always much larger than the experimental. This discrepancy would seem to indicate that the region of the effective potential in scattering experiments cannot be fully represented by only a R^{-6} potential. Higher order terms of $E_2(R)$, i.e., R^{-8} and R^{-10} terms may not be negligible. The one-center method could possibly offer a solution to this problem because these terms can be calculated by this procedure. Combined with values for the repulsive interaction we can obtain a reasonable theoretical intermolecular potential at least for rare gas systems.

APPENDIX A

USE OF A SUM RULE TO DEVELOP DIFFERENTIAL EQUATIONS FROM THE POLARIZABILITY EXPRESSION

We want to rewrite equation (49) in the text into a simpler form, i.e., a form where the infinite summation is no longer present. We have

$$\alpha_\ell(u) = -2\Sigma'_s \frac{(E^s-E^o)\langle\Phi^s|W_\ell|\Phi^o\rangle\langle\Phi^s|W_\ell|\Phi^o\rangle}{(E^s-E^o)^2 - u^2} \tag{49}$$

Since Φ^s is an exact eigenstate of the atom, we know that

$$(E^s-E^o)\langle\Phi^s|W_\ell|\Phi^o\rangle = \langle\Phi^s|(H-E^o)W_\ell|\Phi^o\rangle \tag{A-1}$$

Thus, we have

$$\langle\Phi^s|(H-E^o)W_\ell|\Phi^o\rangle = \langle\Phi^s|[H,W_\ell]\Phi^o\rangle \tag{A-2}$$

where $[H,W_\ell]$ is simply the usual commutator

$$\langle\Phi^s|[H,W_\ell]\Phi^o\rangle = \langle\Phi^s|[-\tfrac{1}{2}\nabla^2,W_\ell]\Phi^o\rangle \tag{A-3}$$

$$= \langle\Phi^s|-\tfrac{1}{2}[\Phi^o\vec{\nabla}^2W_\ell+2\vec{\nabla}W_\ell\ \vec{\nabla}\Phi^o]\rangle \tag{A-4}$$

$$= -\tfrac{1}{2}\langle\Phi^s|\nabla^2W_\ell|\Phi^o\rangle - \langle\Phi^s|\vec{\nabla}W_\ell\cdot\vec{\nabla}|\Phi^o\rangle \tag{A-5}$$

since all other terms in H commute with W.

$$\nabla^2 W_\ell = \frac{1}{r}\frac{\partial^2}{\partial r^2}[-r^{\ell+1}P_\ell(\cos\theta)] + \frac{\ell(\ell+1)}{r^2}\, r^\ell P_\ell(\cos\theta)$$

$$= [\ell(\ell+1)-\ell(\ell+1)]r^{\ell-2}P_\ell(\cos\theta) \;=\; 0 \qquad \text{(A-6)}$$

Therefore

$$(E^s-E^o)\langle\Phi^s|W_\ell|\Phi^o\rangle = -\langle\Phi^s|\vec{\nabla}W_\ell\cdot\vec{\nabla}|\Phi^o\rangle \qquad \text{(A-7)}$$

Substituting (A-7) into equation (49), we get either

$$\alpha_\ell(u) \;=\; 2\Sigma'_s \frac{\langle\Phi^o|W_\ell|\Phi^s\rangle\langle\Phi^s|\vec{\nabla}W_\ell\cdot\vec{\nabla}|\Phi^o\rangle}{(E^s-E^o)^2+u^2} \qquad \text{(A-8)}$$

or

$$\alpha_\ell(u) = 2\Sigma'_s \frac{\langle\Phi^s|\vec{\nabla}W_\ell\cdot\vec{\nabla}|\Phi^o\rangle\langle\Phi^o|W_\ell|\Phi^s\rangle}{(E^s-E^o)^2+u^2} \qquad \text{(A-9)}$$

To simplify equations (A-8) and (A-9) we need to use a sum rule developed by A. Dalgarno and J. T. Lewis.*

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*See A. Dalgarno, "Quantum Theory", Vol. 1, Page 185, edited by D. R. Bates; J. O. Hirschfelder, W. B. Brown, and S. T. Epstein, Advances in Quantum Chemistry, Vol.1, 1964, Page 338, for another development.

$$\sum_s{}' \frac{\langle \phi_n|\alpha|\phi_t\rangle\langle\phi_t|\beta|\phi_m\rangle}{E_t-E_m+\omega} = \langle\phi_n|\alpha|F\phi_m\rangle - \langle\phi_n|\alpha|\phi_m\rangle\langle\phi_m|F\phi_m\rangle \qquad \text{(A-10)}$$

where F is a solution of

$$(H-E_m+\omega)F\phi_m = \beta\phi_m - \langle\phi_m|\beta|\phi_m\rangle\phi_m + \omega\langle\phi_m|F\phi_m\rangle\phi_m \quad . \qquad \text{(A-11)}$$

Using equation (A-10), equation (A-8) becomes

$$\alpha_\ell(u) = 2\langle\Phi^o|W_\ell|F\Phi^o\rangle - 2\langle\Phi^o|W_\ell|\Phi^o\rangle\langle\Phi^o|F\Phi^o\rangle \quad . \qquad \text{(A-12)}$$

For our system $\langle\Phi^o|W_\ell|\Phi^o\rangle = 0$. Letting $F\Phi^o = \Theta_\ell$, we get

$$\alpha_\ell(u) = 2\langle\Phi^o|W_\ell|\Theta_\ell\rangle \qquad \text{(A-13)}$$

which is equation (51) in the text.

From equation (A-11), Θ_ℓ is the solution to

$$[(H-E^o)^2+u^2]\Theta_\ell = \vec{\nabla}W_\ell\cdot\vec{\nabla}\Phi^o - \langle\Phi^o|\vec{\nabla}W_\ell\cdot\vec{\nabla}|\Phi^o\rangle\Phi^o + u^2\langle\Phi^o|\Theta_\ell\rangle\Phi^o \qquad \text{(A-14)}$$

or equation (52) in the text .

Following the same procedure, equation (A-9) becomes

$$\alpha_\ell(u) = 2\langle\Phi^o|\vec{\nabla}W_\ell\cdot\vec{\nabla}|\Psi_\ell\rangle \qquad \text{(A-15)}$$

which is equation (53) in the text where Ψ_ℓ is solution to

$$[(H-E^{o})^{2}+u^{2}]\Psi_{\ell} = W_{\ell}\Phi^{o}+u^{2}\langle\Phi^{o}|\Psi_{\ell}\rangle\Phi^{o} \qquad \text{(A-16)}$$

or equation (54) in the text.

APPENDIX B

EXPANSION OF THE COMMUTATION RELATION AND THE PRESENTATION OF THE GENERAL $B_{jk}^{(\ell)}$, $C_j^{(\ell)}$, and $F_{ij}^{(\ell)}$ TERMS

From equation (109), we have

$$\langle (h_i^o - \varepsilon_i^o) f_{ij}^{(\ell)} \varphi_i^o | (h_i^o - \varepsilon_i^o) f_{ik}^{(\ell)} \varphi_i^o \rangle = \langle [-\tfrac{1}{2}\nabla_i^2, f_{ij}^{(\ell)}] \varphi_i^o | [-\tfrac{1}{2}\nabla_i^2, f_{ik}^{(\ell)}] \varphi_i^o \rangle \quad \text{(B-1)}$$

We first write φ_i^o as a product of an angular and a radial part:

$$\varphi_i^o = Y_{\ell m} \varphi_i^o(r) \quad \text{(B-2)}$$

Now we expand the bra of equation (B-1)

$$[-\tfrac{1}{2}\nabla^2, f]\varphi = [-\tfrac{1}{2}\nabla^2, f] Y_{\ell m} \varphi(r) = -\tfrac{1}{2}(\nabla^2 f) Y_{\ell m} \varphi(r) - \vec{\nabla} f \cdot \vec{\nabla} [Y_{\ell m} \varphi(r)]$$

$$= -\tfrac{1}{2}(\nabla^2 f) Y_{\ell m} \varphi(r) - \varphi(r) \vec{\nabla} f \cdot \vec{\nabla} Y_{\ell m} - Y_{\ell m} \vec{\nabla} f \cdot \vec{\nabla} \varphi(r) \quad \text{(B-3)}$$

where subscripts have been eliminated for simplicity. The first term on the right-hand side of equation (B-3) is then expanded

$$-\tfrac{1}{2}(\nabla^2 f) Y_{\ell m} \varphi(r) = -\tfrac{1}{2}(\nabla^2 Y_{\ell m}) f \varphi(r) - \tfrac{1}{2}(\nabla^2 f) Y_{\ell m} \varphi(r) - \varphi(r) \vec{\nabla} f \cdot \vec{\nabla} Y_{\ell m} \quad \text{(B-4)}$$

which can be rearranged to give

$$-\tfrac{1}{2}(\nabla^2 f) Y_{\ell m} \varphi(r) = -\tfrac{1}{2}\nabla^2 (f Y_{\ell m}) \varphi(r) + \tfrac{1}{2}(\nabla^2 Y_{\ell m}) f \varphi(r) + \varphi(r) \vec{\nabla} f \cdot \vec{\nabla} Y_{\ell m} \quad \text{(B-5)}$$

Substituting equation (B-5) into equation (B-3), we get

$$[-\tfrac{1}{2}\nabla^2, f]\varphi = -\tfrac{1}{2}\nabla^2(fY_{\ell m})\varphi(r)+\tfrac{1}{2}(\nabla^2 Y_{\ell m})f\varphi(r)-Y_{\ell m}\vec{\nabla}f\cdot\vec{\nabla}\varphi(r) \qquad \text{(B-6)}$$

which reduces to

$$[-\tfrac{1}{2}\nabla^2, f]\varphi = -\tfrac{1}{2}\nabla^2(F)\varphi(r) - \frac{\ell(\ell+1)}{2r^2} F\varphi(r) - \vec{\nabla}_r F\cdot\vec{\nabla}\varphi(r) \qquad \text{(B-7)}$$

which is equation (111) in the text.

Substitution of equation (B-7) into equations (106) and (107) we find the general equations for $B_{jk}^{(\ell)}$ and $C_j^{(\ell)}$:

$$B_{jk}^{(\ell)} = \tfrac{1}{4}\langle\varphi\nabla^2 F_j^{(\ell)}|\varphi\nabla^2 F_k^{(\ell)}\rangle + \tfrac{1}{4}\ell(\ell+1)\langle\varphi\nabla^2 F_j^{(\ell)}|r^{-2}F_k^{(\ell)}\varphi\rangle$$

$$+ \tfrac{1}{2}\langle\varphi\nabla^2 F_j^{(\ell)}|\vec{\nabla}_r F_k^{(\ell)}\cdot\vec{\nabla}\varphi\rangle + \tfrac{1}{4}\ell(\ell+1)\langle\varphi\nabla^2 F_k^{(\ell)}|r^{-2}F_j^{(\ell)}\varphi\rangle$$

$$+ \tfrac{1}{4}[\ell(\ell+1)]^2\langle r^{-2}F_j^{(\ell)}\varphi|r^{-2}F_k^{(\ell)}\varphi\rangle + \langle\vec{\nabla}_r F_j^{(\ell)}\cdot\vec{\nabla}\varphi|\vec{\nabla}_r F_k^{(\ell)}\cdot\vec{\nabla}\varphi\rangle$$

$$+ \tfrac{1}{2}\ell(\ell+1)\langle r^{-2}F_j^{(\ell)}\varphi|\vec{\nabla}_r F_k^{(\ell)}\cdot\vec{\nabla}\varphi\rangle + \tfrac{1}{2}\langle\varphi\nabla^2 F_k^{(\ell)}|\vec{\nabla}F_j^{(\ell)}\cdot\vec{\nabla}\varphi\rangle$$

$$+ \tfrac{1}{2}\ell(\ell+1)\langle r^{-2}F_k^{(\ell)}\varphi|\vec{\nabla}_r F_j^{(\ell)}\cdot\vec{\nabla}\varphi\rangle + \sum_n(\varepsilon_n-\varepsilon_i)\{\tfrac{1}{2}\langle\nabla^2 F_j^{(\ell)}\varphi,\varphi_n\rangle\langle F_k^{(\ell)}\varphi,\varphi_n\rangle$$

$$+ \frac{\ell(\ell+1)}{2}\langle r^{-2}F_j^{(\ell)}\varphi,\varphi_n\rangle\langle F_k^{(\ell)}\varphi,\varphi_n\rangle + \langle\vec{\nabla}_r F_j^{(\ell)}\cdot\vec{\nabla}\varphi,\varphi_n\rangle\langle F_k^{(\ell)}\varphi,\varphi_n\rangle$$

$$+ \tfrac{1}{2}\langle\nabla^2 F_k^{(\ell)}\varphi,\varphi_n\rangle\langle F_j^{(\ell)}\varphi,\varphi_n\rangle + \frac{\ell(\ell+1)}{2}\langle r^{-2}F_k^{(\ell)}\varphi,\varphi_n\rangle$$

$$+ \langle\vec{\nabla}_r F_k^{(\ell)}\cdot\vec{\nabla}\varphi,\varphi_n\rangle\langle F_j^{(\ell)}\varphi,\varphi_n\rangle + (\varepsilon_n-\varepsilon_i)\langle F_j^{(\ell)}\varphi,\varphi_n\rangle\langle F_k^{(\ell)}\varphi,\varphi_n\rangle\}$$

$$+ u^2\{\langle F_j^{(\ell)}\varphi|F_k^{(\ell)}\varphi\rangle - \sum_n[\langle F_j^{(\ell)}\varphi,\varphi_n\rangle\langle F_k^{(\ell)}\varphi,\varphi_n\rangle$$

$$+ \langle\varphi_n,F_k^{(\ell)}\rangle\langle F_j^{(\ell)}\varphi,\varphi_n\rangle - \langle\varphi_n,\varphi_n\rangle\langle F_j^{(\ell)}\varphi,\varphi_n\rangle]\} \qquad \text{(B-8)}$$

$$C_j^{(\ell)} = -\tfrac{1}{2}\langle\nabla^2 F_j^{(\ell)}\varphi|W_\ell\varphi\rangle - \frac{\ell(\ell+1)}{2}\langle r^{-2}F_j^{(\ell)}\varphi|W_\ell\varphi\rangle - \langle\vec{\nabla}_r F_j^{(\ell)}\cdot\vec{\nabla}|W_\ell\varphi\rangle$$

$$- \sum_n(\varepsilon_n-\varepsilon_i)\langle W_\ell\varphi,\varphi_n\rangle\langle F_j^{(\ell)}\varphi,\varphi_n\rangle \qquad \text{(B-9)}$$

The sum over n extends over all occupied orbitals. In above equations $\varphi = \varphi_i^o(r)$, $F_j^{(\ell)} = F_{ij}^{(\ell)} = r_i^\ell P_\ell(\cos\theta_i)Y_{\ell m}$, and $\varphi_n^o = \varphi_n^o(\theta,\phi,r)$.

The various $F_{ij}^{(\ell)}$'s used in our calculations are given below: j starts at 1 and is allowed to become as large a value as seems necessary for convergence.

	Excitation	$F_{ij}^{(\ell)}$
Dipole	$s \rightarrow p$	$r^j Y_{10}$
	$p_{\pm 1} \rightarrow d_{\pm 1}$	$r^j Y_{2\pm 1}$
	$p_0 \rightarrow s$	$r^{j-1} Y_{00}$
	$p_0 \rightarrow d$	$r^j Y_{20}$
Quadrupole	$s \rightarrow d$	$r^{j+1} Y_{20}$
	$p_{\pm 1} \rightarrow p_{\pm 1}$	$r^j Y_{1\pm 1}$
	$p_{\pm 1} \rightarrow f_{\pm 1}$	$r^{j+1} Y_{3\pm 1}$
	$p_0 \rightarrow p_0$	$r^j Y_{10}$
	$p_0 \rightarrow f_0$	$r^{j+1} Y_{30}$
Octupole	$s \rightarrow f$	$r^{j+2} Y_{30}$
	$p_{\pm 1} \rightarrow d_{\pm 1}$	$r^j J_{2\pm 1}$
	$p_{\pm 1} \rightarrow g_{\pm 1}$	$r^{j+2} Y_{4\pm 1}$
	$p_0 \rightarrow d_0$	$r^j Y_{20}$
	$p_0 \rightarrow g_0$	$r^{j+2} Y_{40}$

APPENDIX C

EXPANSION OF THE FIRST-ORDER CORRECTION TERMS OF THE POLARIZABILITY

$$\alpha^{1}(u) = \mu[\langle\phi^{(o,1)}|V\text{-}E^{(1,o)}|\phi^{(o,1)}\rangle - \langle\theta^{(o,1)}|V\text{-}E^{(1,o)}|\theta^{(o,1)}\rangle + 2\langle\psi^{(o,o)}|V\text{-}E^{(1,o)}|\psi^{(o,2)}\rangle] \qquad (C\text{-}1)$$

where μ is an ordering parameter and can be set equal to unity at any time we choose. From the text, we have expressions for $\psi^{(o,o)}$, $\phi^{(o,1)}$, $\theta^{(o,1)}$, $\psi^{(o,2)}$, V and $E^{(1,o)}$; namely equations (90), (91), (92), (93), (99), and (115), respectively.

Substitute into equation (C-1) the expressions for V and $E^{(1,o)}$ from equations (99) and (115). Letting $g_{ij} = \frac{1}{r_{ij}}$, we get

$$\begin{aligned}
\alpha^{1}(u) = {} & \langle\phi^{(o,1)}|\sum_{i<j} g_{ij}|\phi^{(o,1)}\rangle \\
& - \langle\phi^{(o,1)}|\langle\varphi_j^{o}(j)|\sum_{i\neq j}(1-P_{ij})g_{ij}|\varphi_j^{o}(j)\rangle_j\phi^{(o,1)}\rangle \\
& + \sum_{i<j}\langle\varphi_i^{o}(i)\varphi_j^{o}(j)|g_{ij}(1-P_{ij})|\varphi_i^{o}(i)\varphi_j^{o}(j)\rangle\langle\phi^{(o,1)}|\phi^{(o,1)}\rangle \\
& - \langle\theta^{(o,1)}|\sum_{i<j} g_{ij}|\theta^{(o,1)}\rangle \\
& + \langle\theta^{(o,1)}|\langle\varphi_j^{o}(j)|\sum_{i\neq j}(1-P_{ij})g_{ij}|\varphi_j^{o}(j)\rangle_j\phi^{(o,1)}\rangle \\
& - \sum_{i<j}\langle\varphi_i^{o}(i)\varphi_j^{o}(j)|g_{ij}(1-P_{ij})|\varphi_i^{o}(i)\varphi_j^{o}(j)\rangle\langle\theta^{(o,1)}|\theta^{(o,1)}\rangle +
\end{aligned}$$

$$+ 2 \sum_{i<j} \langle \psi^{(o,o)} | \sum_{i<j} g_{ij} | \psi^{(o,2)} \rangle$$

$$- 2 \langle \psi^{(o,o)} | \langle \varphi_j^o(j) | \sum_{i \neq j} (1-P_{ij}) g_{ij} | \varphi_j^o(j) \rangle_j | \psi^{(o,2)} \rangle$$

$$+ 2 \sum_{i<j} \langle \varphi_i^o(i) \varphi_j^o(j) | g_{ij}(1-P_{ij}) | \varphi_i^o(i) \varphi_j^o(j) \rangle \langle \psi^{(o,o)} | \psi^{(o,2)} \rangle \quad . \text{(C-2)}$$

Upon substituting the appropriate forms of the functions [equations (90)-(93)] into equation (C-2), we have

$$\alpha^1(u) = \sum_{i<j} \langle \varphi_i^1(i) \varphi_j^o(j) | (1-P_{ij}) g_{ij} | \varphi_i^1(i) \varphi_j^o(j) \rangle$$

$$+ \sum_{i<j} \langle \varphi_i^o(i) \varphi_j^1(j) | (1-P_{ij}) g_{ij} | \varphi_i^o(i) \varphi_j^1(j) \rangle$$

$$- \sum_{i \neq j} \langle \varphi_i^1(i) \varphi_j^o(j) | (1-P_{ij}) g_{ij} | \varphi_j^o(j) \varphi_i^1(i) \rangle$$

$$+ \sum_{i<j} \langle \varphi_i^1(i) \varphi_j^o(j) | (1-P_{ij}) g_{ij} | \varphi_i^o(i) \varphi_j^1(j) \rangle$$

$$+ \sum_{i<j} \langle \varphi_i^o(i) \varphi_j^1(j) | (1-P_{ij}) g_{ij} | \varphi_i^1(i) \varphi_j^o(j) \rangle$$

$$+ 2 \sum_{i<j} \langle \varphi_i^o(i) \varphi_j^o(j) | (1-P_{ij}) g_{ij} | \varphi_i^1(i) \varphi_j^1(j) \rangle$$

$$+ \omega^2 \{ - \sum_{i<j} \langle \theta_i^1(i) \theta_j^o(j) | (1-P_{ij}) g_{ij} | \theta_i^1(i) \theta_j^o(j) \rangle$$

$$- \sum_{i<j} \langle \theta_i^o(i) \theta_j^1(j) | (1-P_{ij}) g_{ij} | \theta_i^o(i) \theta_j^1(j) \rangle +$$

$$+ \sum_{i\neq j} \langle \theta_i^1(i)\theta_j^0(j) | (1-P_{ij})g_{ij} | \theta_j^0(j)\theta_i^1(i) \rangle$$

$$- \sum_{i<j} \langle \theta_i^1(i)\theta_j^0(j) | (1-P_{ij})g_{ij} | \theta_i^0(i)\theta_j^1(j) \rangle$$

$$- \sum_{i<j} \langle \theta_i^0(i)\theta_j^1(j) | (1-P_{ij})g_{ij} | \theta_i^1(i)\theta_j^0(j) \rangle$$

$$+ 2 \sum_{i<j} \langle \theta_i^0(i)\theta_j^0(j) | (1-P_{ij})g_{ij} | \theta_i^1(i)\theta_j^1(j) \rangle] \quad . \quad \text{(C-3)}$$

Rearranging and cancelling like terms, we get the following simple expression for $\alpha^1(u)$:

$$\alpha^1(u) = 4 \sum_{i<j} \langle \varphi_i^1(i)\varphi_j^0(j) | (1-P_{ij})g_{ij} | \varphi_i^0(i)\varphi_j^1(j) \rangle \quad \text{(C-4)}$$

the only unknown functions being φ_i^1 and φ_j^1, which are obtained from equation (104).

APPENDIX D

REPRINT FOR TWO ELECTRON ATOMS

Multipole Polarizabilities and London Dispersion Forces of He and Li^+ Using Double Perturbation Theory

J. T. Broussard and Neil R. Kestner, J. Chem. Phys., 53, 1507(1970)

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Multipole Polarizabilities and London Dispersion Forces of He and Li^+ Using Double Perturbation Theory*

J. T. BROUSSARD† AND NEIL R. KESTNER‡
Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803
(Received 13 April 1970)

Following the double perturbation-theory method used by Deal, Kestner, and Young, dipole, quadrupole, and octopole polarizabilities with and without correlation have been calculated for He and Li^+ at imaginary frequencies. Also calculated are the C_6, C_8, and C_{10} coefficients for He–He and Li^+–Li^+ interactions with and without correlation for several Hartree–Fock-type wavefunctions.

INTRODUCTION

In previous work[1,2] it was shown that by using double perturbation theory, multipole polarizabilities can be calculated with relative ease of computation and only a slight loss in accuracy. Since correlation is an integral part of the calculations, difficulties are inherent whenever more rigorous methods[3] such as the coupled and uncoupled Hartree–Fock procedures are used to calculate atomic properties. The more rigorous methods require many self-consistency requirements, e.g., the solution of N-coupled one-electron equations and the knowledge of wavefunctions including correlation, whereas double perturbation theory can be used to obtain the effects of correlation on polarizability even though wavefunctions including correlation are not known. Also, using double perturbation theory, no two-electron equations need to be solved; they are simply products of the two one-electron solutions in the cases of He and Li^+.

Once the polarizabilities have been calculated, the interaction between two atoms can be written as the integral over imaginary frequencies of the product of the frequency-dependent polarizabilities of the two atoms.[4]

BASIC METHOD

Following the derivation of an earlier paper[1,5] we consider a system with an initial time-dependent wavefunction $\psi^0\exp(-iE^0t)$, a Hamiltonian H^0, and energy E^0 subject to two perturbations; one, μV, time independent, and the other, $\lambda\omega\exp(-\omega t)$, time dependent with imaginary frequencies $i\omega$, where λ and μ are ordering parameters. The perturbation equations one finds are as follows: If we let

$$\Psi=\Psi^0+\lambda\Psi'+\cdots, \tag{1}$$

$$\Psi^0=(\psi^0+\mu\psi'+\cdots)\exp(-iEt), \tag{2}$$

$$\Psi'=[(\phi^0+i\theta^0)+\mu(\phi'+i\theta')+\cdots]\exp[-(iE+\omega)t], \tag{3}$$

then

$$(H^0-E^0)\phi^0-\omega\theta^0+W\psi^0=0, \tag{4}$$

$$(H^0-E^0)\theta^0+\omega\phi^0=0, \tag{5}$$

$$(H^0-E^0)\phi'-\omega\theta'+(V-E')\phi^0+W\psi'=0, \tag{6}$$

$$(H^0-E^0)\theta'+\omega\phi'+(V-E')\theta^0=0. \tag{7}$$

It is now required that ψ^0 be the Hartree–Fock wavefunction, V is the correction for electron correlation, and W the external perturbation

$$W=-\sum_{i=1}^{N} r_i^l P_l(\cos\theta_i) \tag{8}$$

for an N-electron system where 2^l is equal to the multipole being used. ϕ^0 and θ^0 can be obtained by solving the differential equations

$$[(H^0-E^0)^2+\omega^2]\phi^0+(H^0-E^0)W\psi^0=0, \tag{9}$$

$$[(H^0-E^0)^2+\omega^2]\theta^0-\omega W\psi^0=0, \tag{10}$$

or by minimizing the variational expressions[6]

$$J_1=\langle\phi^0\,|(H^0-E^0)^2+\omega^2\,|\,\phi^0\rangle+2\langle\phi^0\,|(H^0-E^0)W\,|\,\psi^0\rangle, \tag{11}$$

$$J_2=\langle\theta^0\,|(H^0-E^0)^2+\omega^2\,|\,\theta^0\rangle-2\omega\langle\theta^0\,|\,W\,|\,\psi^0\rangle. \tag{12}$$

TABLE I. Polarizabilities of helium at imaginary frequencies (in atomic units) $\alpha(i\omega)$.[a]

	Dipole		Quadrupole		Octopole	
ω	No correlation	With correlation	No correlation	With correlation	No correlation	With correlation
0.0	1.4870	1.2942	2.361	2.326	10.054	10.031
0.10	1.4705	1.2812	2.343	2.310	9.993	9.971
0.30	1.3521	1.1869	2.215	2.184	9.541	9.519
0.50	1.1702	1.0396	2.003	1.976	8.766	8.747
0.80	0.8932	0.8091	1.639	1.619	7.370	7.353
1.00	0.7396	0.6778	1.413	1.397	6.460	6.445
3.00	0.1706	0.1653	0.385	0.383	1.884	1.881
5.00	0.0701	0.0691	0.164	0.163	0.809	0.808
7.00	0.0377	0.0373	0.0888	0.0886	0.439	0.439
10.00	0.0191	0.0190	0.0452	0.0451	0.223	0.223

[a] Three-term Hartree–Fock orbitals from Ref. 7.

TABLE II. Polarizabilities of Li^+ at imaginary frequencies (in atomic units) $\alpha(i\omega)$.[a]

	Dipole		Quadrupole		Octopole	
ω	No correlation	With correlation	No correlation	With correlation	No correlation	With correlation
0.0	0.2049	0.1878	0.1132	0.1121	0.1662	0.1660
0.10	0.2046	0.1876	0.1130	0.1120	0.1661	0.1659
0.30	0.2023	0.1855	0.1122	0.1112	0.1652	0.1649
0.50	0.1977	0.1816	0.1107	0.1096	0.1633	0.1631
0.80	0.1876	0.1729	0.1070	0.1061	0.1590	0.1587
1.00	0.1792	0.1656	0.1039	0.1030	0.1552	0.1550
3.00	0.0937	0.0890	0.0651	0.0646	0.1041	0.1040
5.00	0.0502	0.0486	0.0388	0.0385	0.0650	0.0650
7.00	0.0302	0.0295	0.0247	0.0246	0.0423	0.0423
10.00	0.0166	0.0164	0.0141	0.0141	0.0247	0.0247

[a] Three-term Hartree–Fock from Ref. 7.

TABLE III. Static polarizabilities and coefficients for He using Hartree–Fock orbitals.[a]

	Polarizabilities			Dispersion interactions			
						$C_{1\ell}$[b]	
	Dipole	Quadrupole	Octopole	C_6	C_8	C_{qq}	C_{d0}
No correlation	1.4870	2.3606	10.0537	1.664	14.65	60.87	121.50
With correlation	1.2942	2.3265	10.0308	1.335	13.00	59.37	109.05
	1.384[e]				13.18[f]		
Literature value		$2.326 \leq \alpha_q < 2.359$[e]		1.471[d]		59.39[f]	110.44[f]
	1.3796[d]				14.1[d,g]		

[a] Using three-term orbitals from Ref. 7.
[b] C_{qq} is the quadrupole–quadrupole contribution while C_{d0} is the dipole–octopole contribution.
[c] C. Schwartz, Phys. Rev. 123, 1700 (1961).
[d] W. D. Davison, Proc. Phys. Soc. (London) 87, 133 (1966).
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[f] A. Dalgarno and A. L. Stewart, Proc. Roy. Soc. (London), A238, 269 (1956).
[g] Best estimate, see A. Dalgarno, Advan. Chem. Phys. 12, 155 (1967).

TABLE IV. Static polarizabilities and coefficients for Li^+ using Hartree–Fock orbitals.[a]

	Polarizabilities			Dispersion interactions			
						C_{10}[b]	
	Dipole	Quadrupole	Octopole	C_6	C_8	C_{qq}	C_{30}
No correlation	0.2049	0.1132	0.1662	0.869	0.270	0.397	0.777
With correlation	0.1878	0.1121	0.1660	0.757	0.251	0.391	0.726
Literature value	0.1922	$0.1118<\alpha_q<0.1138$[a]					

[a] Orbitals from Ref. 7.
[b] A. Dalgarno, Advan. Phys. 11, 304 (1962).
[c] C_{qq} is the contribution of quadrupole–quadrupole interactions, while C_{30} is the dipole–octopole contribution.

The polarizability to first order in electron correlation is

$$-\tfrac{1}{2}\alpha_l(i\omega)=\langle\psi^0\mid W\mid\phi^0\rangle+\mu[\langle\psi'\mid W\mid\phi^0\rangle+\langle\psi^0\mid W\mid\phi'\rangle]. \quad (13)$$

ψ' and ϕ' involve knowledge of the atomic wavefunction including correlation and thus are difficult to determine in large systems. Using our set of equations we can eliminate these by defining a function of second order in the one-electron perturbation. This function, θ_+, is defined by the equation[5]

$$(H^0-E^0)\theta_+=-W\phi^0+\langle\phi^0\mid W\mid\psi^0\rangle\psi^0 \quad (14)$$

from which is obtained

$$-\tfrac{1}{2}\alpha_l(i\omega)=\langle\psi^0\mid W\,\phi^0\rangle+\mu(\langle\phi^0\mid V-E'\mid\phi^0\rangle-\langle\theta^0\mid V-E'\mid\theta^0\rangle+2\langle\psi^0\mid V-E'\mid\theta_+\rangle). \quad (15)$$

It has been shown[2] that θ_+ is determined by θ^0 and ϕ^0. This brings about a simplification in Eq. (16). We define

$$\phi_0=\sum_{i=1}^{N}\sum_{j=1}^{m}Y_jr_i^jP_l(\cos\theta_i)\psi^0=\sum_i F_i(r_i\theta_i)\psi^0, \quad (16)$$

$$\theta^0=\sum_{i=1}^{N}\sum_{j=1}^{m}X_{j\omega}r_i^jP_l(\cos\theta_i)\psi^0=\sum_i G_i(r_i\theta_i)\omega\psi^0, \quad (17)$$

then

$$\theta_+=[F_1F_2+\omega^2G_1G_2]\psi^0 \quad (18)$$

for a two-electron system ($N=2$).

The above functions are substituted into Eq. (15) to obtain for two-electron systems in particular

$$-\tfrac{1}{2}\alpha_l(i\omega)=-\sum_{i=1}^{2}\sum_{j=l}^{m}Y_j\langle r_i^{j+l}P_l^2(\cos\theta_i)\phi^2(r_i)\rangle+4\sum_{j=l}^{m}\sum_{k=l}^{m}Y_jY_k\times\iint\frac{[r_1^jP_l(\cos\theta_1)\phi^2(r_1)][r_2^kP_l(\cos\theta_2)\phi^2(r_2)]}{r_{12}}d\tau_1d\tau_2. \quad (19)$$

The coefficient C_{AB} for interactions between atoms A and B which varies as $r^{-2(l+L)-2}$ is related to the various $\alpha(i\omega)$ as[6]

$$C_{AB}(l,L)=\frac{(2l+2L)!}{4(2l)!(2L)!}\frac{2}{\pi}\int_0^\infty\alpha_{lA}(i\omega)\alpha_{LB}(i\omega)d\omega. \quad (20)$$

Equation (20) is only valid for the Hartree–Fock result in which V is the electron–electron repulsion minus the local Hartree–Fock potential, i.e.,

$$V=r_{12}^{-1}-\int[\mid\phi(r_1)\mid^2/r_{12}]dr_1-\int[\mid\phi(r_2)\mid^2/r_{12}]dr_2, \quad (21)$$

ϕ is the Hartree–Fock orbital. We have calculated polarizabilities using two-, three-, four-, and five-term Hartree–Fock wavefunctions. The Bagus–Gilbert three-term[7] results are equivalent to the five-term Clementi result[8] to four significant figures. The two-term results are 0.5% low for dipole and 6% low for octopole polarizabilities. Dispersion interactions are low by the sum of the errors in the static polarizabilities. Thus we list only the one basis function in the tables.

To evaluate Eq. (20) polarizabilities were calculated to frequencies large enough to use the sum rule procedure of Mavroyannis and Stephens[4] to extend the numerical integration to infinite frequency. All computations were performed with a self-contained computer program with convergence being very rapid. The results listed in the tables are for $m=5+l$, which are essentially no different from those of $m=3+l$. For all polarizabilities a 6×6 determinant was solved for the Y_j's.

DISCUSSION

The numerical results of this paper are presented in Tables I–IV.

The purpose of this paper was to extend the method of the previous paper[1] to higher multipole polarizabilities, i.e., quadrupole and octopole using the same method as before, however, with a significant simplification in the determination of θ_+ [Eq. (18)]. In the two procedures the dipole polarizabilities without correlation agree, but do not agree as well for the cases with correlation. In the derivation of Eq. (19) it was found that to first order in electron correlation the terms proportional to ω^{-4} vanish leaving only a term proportional to ω^{-1}. In the previous paper[1] terms proportional to ω^{-4} as well as ω^{-2} were erroneously present. Correlation corrections are larger by about 7% or about 3% further

TABLE V. Comparison of several methods of obtaining helium-atom polarizabilities at zero frequency.

Method	Dipole polarizability (in units of a_0^3)	Quadrupole polarizability (in units of a_0^5)
Method c (Epstein and Johnson)[a]	1.242	2.210
Geometric extrapolation of method c[b]	1.319	2.329
This paper	1.294	2.326
Geometric extrapolation of this paper's results[b]	1.316	2.326
Coupled perturbation theory[c]	1.323	2.331
Exact[d]	1.380	2.440

[a] Reference 15.
[b] The geometric approximation is discussed in Ref. 14 in the text. It is equivalent to a [10] Padé approximant.
[c] P. W. Langhoff, M. Karplus, and R. P. Hurst, J. Chem. Phys. 44, 505 (1966).
[d] W. D. Davison, Ref. 12.

from experimental values than in the previous paper when using a two-term Hartree–Fock wavefunction. The same is true for the C_6 coefficient. Using three- or more-term Hartree–Fock wavefunctions, the difference is slightly less.

Values without correlation for helium have been previously published by Karplus and Kolker.[9] Their values, $\alpha(0)=1.480$ and $C_6=1.6551$, compare well with our values using either the Bagus–Gilber or Clementi orbitals. Also using the many-electron theory,[10] a value of $C_6=1.6443$ was obtained using Green's orbitals without correlation.

Dalgarno and Stewart have calculated higher terms of the series expansion of $E_2(R)$ with the result that for He–He,[11]

$$E_2(R)=-\left[\frac{1.376}{R^6}+\frac{13.18}{R^8}+\frac{110.44+59.39}{R^{10}}+O(R^{-12})\right],$$

the dipole–octopole term contributing 110.44 to the R^{-10} coefficient and the quadrupole-quadrupole term contributing 59.39. Two-center calculations[12] give a value of -14.09 for the R^{-8} coefficient. The best estimate of $E_2(R)$ for He–He is[13]

$$E_2(R)=-\left[\frac{1.471}{R^6}+\frac{14.1}{R^8}+\frac{182}{R^{10}}+O(R^{-12})\right].$$

These values for He–He coefficients agree quite well with our calculations using double perturbation theory, which offers a simple and speedy method for doing such calculations. For comparison our results are

$$E_2(R)=-\left[\frac{1.335}{R^6}+\frac{13.00}{R^8}+\frac{109.05+59.37}{R^{10}}+\cdots\right].$$

Finally, in Table V we investigate the use of the geometric approximation,[14] i.e., we assume that our series [$\alpha^{(0)}$ is the calulated value without any electron correlation corrections]

$$\alpha(0)=\alpha^{(0)}+\Delta\alpha \tag{22}$$

are the first terms in the more general result

$$\alpha=\frac{\alpha^{(0)}}{1-(\Delta\alpha/\alpha^{(0)})}. \tag{23}$$

This is equivalent to using the rather simple [10] Padé approximant. We compare Eqs. (22)–(23) with the coupled perturbation theory results. It is observed that although Epstein and Johnson[15] used an alternative approach, their extrapolated value agrees with ours and, more importantly, with the coupled result. That such a result should be found will be justified in other articles.[16]

The sign of the correlation correction in our approach is of interest in the higher multipole polarizabilities since it appears, at least for the quadrupole case, that the corrections make the agreement with the best values worse. A possible reason for this is that the second-order corrections could be large and of opposite sign. This could be true since one can have two correlation corrections, each proportional to $Y_{10}(\theta,\phi)$ as opposed to one of the $Y_{20}(\theta,\phi)$ type. We know the former are larger and possibly even their second-order effect is large. Calculations along this line are needed. Calculations are also under way to apply this method to neon and other larger atoms.

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† NDEA and NASA Predocteral Fellow.
‡ Alfred P. Sloan Fellow.
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VITA

Joseph Tracy Broussard was born in the rural area of Gueydan, Louisiana on September 1, 1944. He attended Gueydan Elementary, and was graduated from Gueydan High in May, 1962. He received his B.S. in Chemistry from the University of Southwestern, Lafayette, Louisiana in June 1966. Currently, he is a candidate for the Doctor of Philosophy degree in Chemistry at Louisiana State University.

He is married to the former Andrea C. Hebert, also of Gueydan, and has a daughter, Tracey Michelle, born December 15, 1966.

EXAMINATION AND THESIS REPORT

Candidate: Joseph Tracy Broussard

Major Field: Chemistry

Title of Thesis: Multipole Polarizabilities and Long Range Interatomic Forces for Two and Ten Electron Atoms

Approved:

Neil R. Kestner
Major Professor and Chairman

Max Goodrich
Dean of the Graduate School

EXAMINING COMMITTEE:

Robert V. Mauman

Philip W. West

James L. Sharton

James Dale Macomber

Date of Examination:

December 15, 1970